A Comparison of the Production of Methanol and Ethanol from Biomass

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For:

International Energy Agency
Agreement on Alternative Motor Fuels

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Preface

The International Energy Agency (IEA) Implementing Agreement on Alternative Motor Fuels was established on May 21, 1984, to foster international cooperation on the development of alcohols, especially methanol, as a transportation fuel.

Production of Alcohols and Other Oxygenates from Fossil Fuels and Renewables, or Annex IV, a component of the Implementing Agreement, was commenced on October 24, 1986. The purpose of Phase I of this Annex was to exchange recent information on the production of alcohols and other oxygenates between the participating countries, in order to review various production methods with the view to identifying potential areas of future development and cooperative research programs. The alcohols covered under this annex include methanol, ethanol, and higher alcohols, and the oxygenates include ethers and other oxygen-containing species that are of use as gasoline additives. This phase identified a number of areas where further study was required. One of these areas was the production of alcohols, especially methanol and ethanol, from biomass. Although there were several studies that dealt with the production of one or the other of the alcohols from biomass, it was found that there was little data, and certainly there were no consistent studies, comparing the production of methanol and ethanol from biomass.

This study addresses this question. It also brings this comparison further, by looking at production processes which are at similar levels of technological development. This is a novel concept in the comparison of technologies.

Annex IV/Phase II has also produced two other studies (*Natural Gas Supply, Demand and Price, and Economic Comparisons of the LNG, Methanol and Synthetic Distillate*, both by Jensen Associates, Inc. of Boston, Massachusetts). A third study (*Greenhouse Gas and Other Emissions to Air Resulting from Ethanol and Methanol Use as Alternative Fuels*, by Ortech International, of Mississauga, Ontario) is in preparation.

Funding of the studies in Annex IV was provided by the following organizations:

- Natural Resources Canada (formerly Department of Energy, Mines and Resources Canada);

- Ecofuel, Italy;

- New Energy and Industrial Technology Development Organization, Japan;

- Swedish National Board for Industrial and Technical Development; and

- Department of Energy, United States of America.

Further information about the studies in Annex IV can be obtained from:

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Abstract

The production of methanol and ethanol from biomass has received extensive research due to concerns over the price and availability of liquid fossil fuels, balance-of-payment problems resulting from oil imports, urban air quality problems, and recent concern over global warming. However, for alcohol fuels to help solve these problems, they must be available in large quantities at a competitive price. Therefore, TDA Research, Inc., under contract to the International Energy Agency's Agreement on Alternative Motor Fuels, carried out a technical and economic analysis of the processes for producing methanol and ethanol from biomass. The objectives were to determine the relative economics of methanol and ethanol production and the ability of process improvements to reduce the cost of production. The study compared processes as a function of the stage of development, using performance and cost data from existing engineering analyses, and adjusting the technical and economic parameters to a common basis. Processes were compared at four different stages of development; i.e., technology which has been 1) commercially demonstrated, 2) demonstrated at the pilot scale, 3) demonstrated at the laboratory scale, and 4) advanced cases which attempt to predict the potential for improvement.

The overall design and efficiency of biochemical conversion processes to produce ethanol are set by the nature of the feedstock and the microorganisms which carry out the conversions. Biomass is made up of three primary fractions: cellulose, hemicellulose and lignin. Cellulose, a polymer of glucose, is difficult to hydrolyze, but once broken down into glucose it is easily fermentable to ethanol. Hemicellulose, composed of xylose, other sugars and organic acids, is easily hydrolyzed but the sugars produced are difficult to ferment. Lignin, a phenolic polymer, cannot be fermented to ethanol. The overall ethanol production process involves hydrolyzing the carbohydrate fractions (cellulose and hemicellulose) to their constituent sugars, fermenting the sugars to produce ethanol, and burning the lignin and other non-fermentable fractions to produce the heat and electricity needed to run the process. Biochemical processes can be very efficient at converting the carbohydrate fraction of the biomass to ethanol, but the inability to convert the lignin and other non-carbohydrate fractions to ethanol limits the potential conversion efficiency to roughly 60%.

The economics of ethanol production are dominated by the effects of conversion efficiency. The commercial-scale process, dilute sulfuric acid hydrolysis with fermentation of the glucose, converts only 20% of the energy content of the feedstock into ethanol due to the low efficiency of the hydrolysis process and the inability to ferment xylose to ethanol. The logen enzymatic hydrolysis process avoids the inefficiencies inherent in dilute acid hydrolysis and makes more efficient use of the cellulose, but still does not ferment the xylose to ethanol (overall efficiency of 30%). In addition, it has high capital costs because it uses large amounts of expensive enzymes to overcome the inhibition of the enzymes by the sugars they produce. The simultaneous hydrolysis and fermentation

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process used in the laboratory and advanced cases reduces the capital cost by reducing the amount of enzyme required, and increases the conversion efficiency (to 39% in the laboratory case) by fermenting the xylose to ethanol. The advanced case is similar to the laboratory case, but assumes that the yields of each of the biochemical steps is increased to near the theoretical limits (conversion efficiency of 50%), and that the capital cost is reduced by increases in reaction rates.

The production of methanol from biomass consists of four major steps: 1) gasification of the biomass to produce raw syngas (a mixture of CO, H_2, CO_2 and H_2O), increasing the H_2/CO ratio by steam reforming and the water gas shift reaction, 3) removing the CO_2, and 4) catalytically converting the CO and H_2 to methanol. The major advantage of the thermochemical processes is that the high-temperature gasification breaks the biomass down into simple molecules. For this reason, the conversion process is relatively unaffected by the detailed structure of the feedstock. Thus, the thermochemical processes are capable of using the entire feedstock, not just the carbohydrate fraction. However, the generation of syngas is very endothermic and requires the input of heat at roughly 1000°C, while the methanol synthesis process is highly exothermic and produces heat at 230-300°C. Because of the temperature mismatch, the heat given off in methanol synthesis cannot be used in gasification and biomass must be burned to provide the energy to drive the process, limiting the overall efficiency to 52-58%.

The commercial-scale technology, Koppers-Totzek gasification followed by low-pressure methanol synthesis, is relatively efficient (40%) but has a very high capital cost. Capital cost reduction is the major issue in thermochemical processes. The high cost comes from the complex and expensive entrained bed gasifer design, the gasifier requirement for very small and dry feedstock particles, and the repeated heating and cooling of the syngas in the cleaning and upgrading process. A major cost item is the cryogenic air separation plant which supplies oxygen to the gasifier to carry out the partial oxidation of the biomass. Pure oxygen must be used because the introduction of nitrogen would greatly increase the cost of the high-pressure methanol synthesis process. The pilot-scale process, the Institute of Gas Technology gasifier combined with the liquid phase methanol synthesis process, uses a less complex and expensive gasifer which does not require an extremely small, dry feedstock. Also, it produces hydrocarbons which can be reformed to produce additional CO and H_2, increasing the efficiency to 45%. The advanced systems use the Battelle-Columbus indirect gasifier and standard low-pressure methanol synthesis technology. In both the base case and advanced processes, the efficiency is increased to 53% due to the reforming of the high hydrocarbon content syngas. Most importantly, the indirectly fired gasifer eliminates the need for an expensive oxygen plant. In the advanced case, the process is further simplified by the use of hot gas clean-up technology which eliminates the need to repeatedly heat and cool the syngas. By simplifying the process and eliminating processing steps, the capital investment is reduced from $62/GJ-yr for the commercial case to $21/GJ-yr in the advanced case.

The cost of methanol and ethanol from biomass for the four cases is:

Table A-1   Cost of methanol and ethanol from biomass.

	Commercial	Pilot	Laboratory	Conceptual
Methanol ($/GJ)	28.5	20.1	14.7	13.1
Ethanol ($/GJ)	33.3	30.0	17.3	12.5

For the commercial and pilot-scale technologies, methanol production is considerably less expensive than ethanol production. This is a direct result of the inability of the early ethanol processes to ferment the xylose fraction to ethanol and the consequent low efficiency. For the more advanced processes there is no significant difference in the economics. This is not surprising as the limiting efficiency of the two processes is essentially identical (90% efficient conversion of 60% of the feedstock is equivalent to 55% conversion on 100% of the feedstock). Significantly, sensitivity analyses show that these conclusion are not sensitive to the assumed feedstock cost, capital recovery factor, or the size of the plant (the three assumptions which have the greatest effect on the process economics).

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Executive Summary

Objective   Over the past two decades extensive research has been carried out on the production of methanol and ethanol from biomass. This interest is a result of concerns over the price and availability of liquid fossil fuels, balance- of-payment problems resulting from expensive oil imports, urban air quality problems created by gasoline and diesel combustion, and recently, concerns over the accumulation of carbon dioxide in the atmosphere and its effect on the global environment. While the production of methanol and ethanol from renewable biomass resources has the potential to alleviate many of these problems, these alcohol fuels must be available in large quantities at a competitive cost if they are to make a significant contribution.

While numerous reports have evaluated various processes for producing either methanol or ethanol, it is still difficult to compare the status of these two technologies. The available studies focus on a single process, and use different technical and economic assumptions, different feedstocks and different plant sizes. The processes evaluated are often at different stages of development, leading one to compare hard numbers with optimistic projections. Unfortunately the lack of a consistent comparison of the various processes makes it difficult to rationally plan national research strategies. Thus, the overall objective of this study is to compare the production of methanol and ethanol on a consistent basis. Specific objectives are to allow the reader to understand: 1) the relative economics of methanol and ethanol processes, 2) the fundamental phenomena which govern the different processes and determine their cost and performance, and 3) what types of process improvements are necessary in order to reduce the cost of producing alcohols from biomass.

Methodology   This study compares processes that are at similar stages of development, uses performance and cost data derived from existing engineering analyses, and adjusts the feedstock cost, plant size, and the technical and economic parameters to a common basis. The processes are evaluated at four different levels of development, *i.e.*, technology which has been: 1) commercially demonstrated, 2) demonstrated at the pilot scale 3) demonstrated at the laboratory scale, and 4) advanced cases which attempt to predict the potential for improvement.

The parameter used to compare different processes is the cost of production of the neat fuel, expressed on an energy basis as United States $/GJ (lower heating value). This figure of merit allows the comparison of fuels with different energy densities. The feedstock was taken as a typical hardwood (red oak or *Quercus rubra*), delivered to the plant gate at a rate of 1,818 tonne/day, and a cost of $46/dry tonne. The plant was designed as a grass-roots facility, with a cost

typical of the midwestern United States, Canada, Western Europe or Japan (approximately 15% higher than United States Gulf Coast capital costs). The cost of production is calculated as:

$$\text{Cost of Production} = \frac{\text{Capital Investment} * \text{CRF} + \text{Annual Operating Expenses}}{\text{Annual Production}}$$

The capital recovery factor (CRF) is a function of the required return on investment, the inflation rate, tax rate, construction time, and plant life. The base case CRF used in this study is 30%, equivalent to an internal rate of return of 15%, with inflation of 3%, and a 20-year plant life. This amounts to a 3.3 year simple payback of the capital investment. Sensitivity analyses were also carried out to determine the effect of plant size, feedstock cost, and the capital recovery factor on the conclusions.

Biochemical Conversion of Biomass to Ethanol The processes used in the biochemical conversion of biomass to ethanol are dictated by the nature of the feedstock. Lignocellulosic biomass (hardwoods, softwoods, and herbaceous crops such as grasses) is made up of three major components: cellulose, hemicellulose and lignin. The largest fraction of biomass is crystalline cellulose (46% by weight in a typical hardwood). This component consists of long chains of glucose molecules that, because of their crystalline packing, are difficult to hydrolyze (break down into simple sugar units), either with enzymes or even with hot acids. However, once the sugars are produced, they are easy to ferment. The second fraction, hemicellulose (30 wt %), consists of polymers of the five-carbon sugar xylose, as well as other sugars and organic acids. Because this fraction is not crystalline, it is easy to hydrolyze to sugars and other small molecules; however, the xylose cannot be fermented to ethanol by standard yeasts, and the organic acids are not fermentable to ethanol. Lignin, the final major fraction (24 wt%), is not a sugar polymer, but is a phenolic polymer which cannot be fermented to ethanol. Lignin accounts for more of the energy content of the wood than is apparent at first glance, since it has a low oxygen content and therefore a high heat of combustion. On an energy basis, cellulose accounts for 42% of the energy content, hemicellulose 26%, and lignin 32%.

A general schematic of the bioconversion of lignocellulosic biomass to ethanol is shown in Figure 1. The feedstock is brought to the plant, and the hemicellulose is hydrolyzed, producing xylose (which is fermented in the more advanced processes). In the case of the enzymatic hydrolysis processes, the hemicellulose hydrolysis also opens the biomass structure to enzymatic attack. The cellulose is then hydrolyzed to glucose, either by acids or enzymes, and the resulting glucose fermented to produce ethanol by the reaction:

$$C_6H_{12}O_6 \rightarrow 2CO_2 + 2C_2H_5OH$$

In the process designs evaluated in this study, the lignin, unfermented sugars, and other organics which are not fermented to ethanol are ultimately dried and
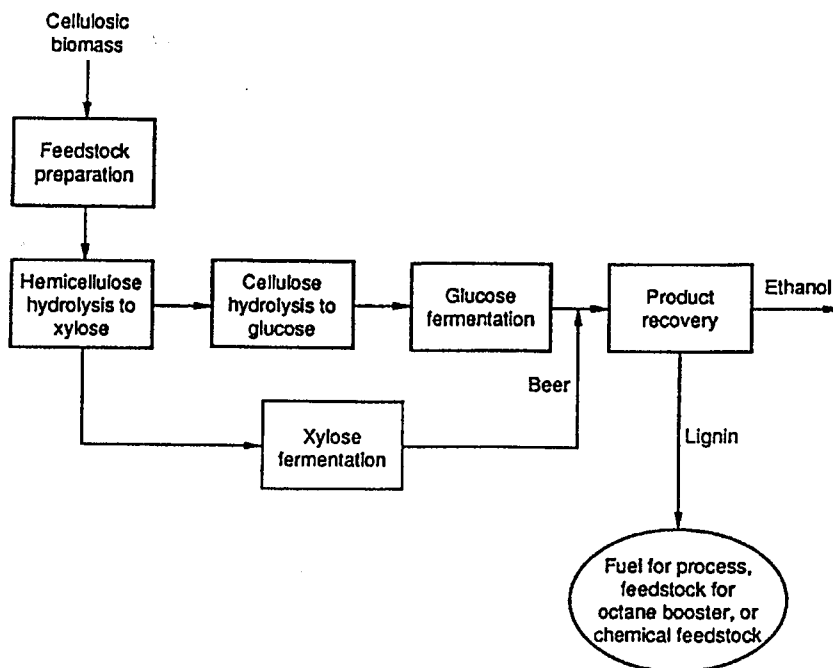
Figure 1   Biochemical conversion of lignocellulosic biomass to ethanol.

burned to produce steam and electricity. As we shall see, the advantages of the bioconversion processes are that the conversions of the individual components are carried out with high efficiency (often approaching 95% energy efficiency). However, the disadvantage is that only the carbohydrate fractions (the cellulose and sugar portion of the hemicellulose) can be converted into ethanol. Thus, the maximum possible energy efficiency is roughly 60%.

The four cases we evaluated were: acid hydrolysis and glucose fermentation (commercial), enzymatic hydrolysis and glucose fermentation (pilot scale), and simultaneous cellulose hydrolysis and fermentation with fermentation of the xylose (laboratory and conceptual cases). The processes are summarized below. The key operating parameters are shown in Table 1, the capital investments by process area are shown in Table 2, and the economics are summarized in Table 3.

Commercial Scale Technology - Dilute Sulfuric Acid (Percolation) Technology with Glucose Fermentation   The percolation dilute acid hydrolysis process was first developed in Germany in the late 1920s, and improvements were made in the United States, Soviet Union, New Zealand, and Switzerland in the 1940's though early 1980s. At one time, over thirty commercial facilities were in operation in the Soviet Union. The major feature of the system is that it uses a semi-batch, high temperature (150-180°C), dilute sulfuric acid (0.5 wt%) process to break down the cellulose and hemicellulose into sugars, followed by a standard yeast-based fermentation process using *S. cerevisiae* to convert the glucose into ethanol. Neither of these processes is very efficient. Because the crystalline cellulose is

Table 1 Performance of biomass to ethanol processes.

	Acid Hydrolysis w/Glucose Fermentation	Enzymatic Hydrolysis w/Glucose Fermentation	Simultaneous Saccharification and Fermentation w/ Xylose Fermentation (Base case)	Simultaneous Saccharification and Fermentation w/ Xylose Fermentation (Advanced Case)
Pre-treatment	None	Auto-hydrolysis	Dilute Acid	Dilute Acid
Hydrolysis Yield C_5 (%) C_6 (%)	55% 63%	-- 85%	87 87	87 --
Fermentation Yield C_5 (%) C_6 (%)	0 85	0 95	90 72	95 90
Energy Efficiency Ethanol (%) Ethanol+ Electricity (%)	20 31.3	30 34	39 43	50 54
Annual Production liters/yr gallons/yr GJ/yr	109 E6 28.9 E6 2.30 E6	168 E6 44.4 E6 3.55 E6	219 E6 57.9 E6 4.63 E6	280 E6 74.1 E6 5.92 E6

so resistant to chemical attack, conditions severe enough to hydrolyze the cellulose are also severe enough to destroy the product sugars. As a result, the yield is relatively low (63% of the potentially fermentable six-carbon sugars are converted to glucose). The liquid hydrolyzate is neutralized and sent to fermentation. As many of the sugar degradation products are toxic, the fermentation efficiency is relatively low (85%), even though the yeast is quite robust. Perhaps most importantly, the xylose fraction is not fermented to ethanol at all. The overall energy efficiency for ethanol production (heating value of the ethanol/heating value of the wood) is only 20%.

The capital investment per unit of production is quite high (because of the low efficiency, the annual output is low). The cost of production is high $33/GJ ($0.70/liter), and is roughly equally split between feedstock costs and charges related to the capital investment.

Pilot Scale Technology - Iogen Enzymatic Hydrolysis Process Because of the low yields inherent in dilute acid hydrolysis processes, most of the research over the past decade has focused on enzymatic hydrolysis processes. The primary advantage is that enzymes hydrolyze the cellulose to glucose without producing any degradation products. Therefore, the yields can be quite high and no toxic byproducts are produced.

Table 2   Capital investment by process area for biomass to ethanol processes.

Section	Acid Hydrolysis w/Glucose Fermentation	Enzymatic Hydrolysis w/Glucose Fermentation	Simultaneous Saccharification and Fermentation w/Xylose Fermentation (Base Case)	Simultaneous Saccharification and Fermentation w/Xylose Fermentation (Advanced Case)
	Investment (million $)			
Feedstock Handling	9.9	14.0	7.2	7.2
Pre-treatment		20.0	23.7	23.7
Enzyme Production		44.0	2.8	1.7
Xylose Fermentation			6.2	3.7
Hydrolysis	22.1	23.0	20.9	8.2
Fermentation	12.6	3.70		
Distillation	20.3	6.05	4.0	4.0
Offsite Tankage	5.8	7.01	4.1	4.6
Environmental Control	18.0	12.0	4.0	3.9
Utilities	46.4	53.3	53.2	46.4
Misc.				2.1
Total Investment	**135.0**	**182**	**128.4**	**105.5**
$/GJ-yr	**58**	**51.2**	**27**	**17.8**

The logen process is a first-generation enzyme-hydrolysis process, and one of only a few which has been run at the pilot scale. This analysis is based on an engineering evaluation carried out for Energy Mines and Resources Canada by Douglas (1989). The logen process uses high pressure steam to hydrolyze the hemicellulose and prepare the biomass for the enzymatic hydrolysis process. The necessary enzymes are produced by a highly mutated fungus (*T. reesei*). Unfortunately, the hydrolysis process requires large amounts of enzymes, because the sugars produced during the hydrolysis inhibit the activity of the enzymes. Thus, the enzyme production process is large and expensive, and the hydrolysis process has a relatively low yield (because high yields would take extremely long times or extremely large amounts of expensive enzyme). The glucose is fermented with 95% efficiency to ethanol by *S. cerevisiae*.

The process efficiency is considerably higher than in the previous case (30% energy conversion to ethanol). However, the capital investment is also quite high, primarily due to the high cost of the enzymes, the long hydrolysis time, and the need for a pretreatment process. However, the capital investment per unit of

Table 3 Cost of production summaries for biomass to ethanol processes.

	Acid Hydrolysis w/Glucose Fermentation	Enzymatic Hydrolysis w/Glucose Fermentation	Simultaneous Saccharification and Fermentation w/Xylose Fermentation (Base Case)	Simultaneous Saccharification and Fermentation w/Xylose Fermentation (Advanced Case)
($/GJ ethanol)				
Raw Materials				
Wood	12.10	3.20	6.05	5.02
Cheese whey		2.10		
Sulfuric acid and lime	1.57		0.23	0.23
Chemicals	0.40	1.20	1.10	1.05
Utilities				
Water	0.14	0.10	0.0	0.0
Electricity	-3.70	-1.0	-0.70	-0.50
Labor	0.71	0.50	0.33	0.30
Maintenance	2.04	2.00	0.40	0.52
Overhead	2.10	2.01	1.10	1.01
Insurance, Property taxes	1.05	1.05	0.43	0.30
Total annual operating costs	16.04	15.00	9.10	7.13
Total capital charges (@30%)	17.53	15.5	8.31	5.34
Cost of Production $/GJ $/l	33.30 0.704	30.05 0.633	17.3 0.366	12.43 0.263

annual capacity is not increased because the investment is spread over a much larger annual production. The cost of ethanol is reduced slightly to $29/GJ or $0.62/liter.

Laboratory and Advanced Technology - Simultaneous Saccharification and Fermentation (SSF) with Xylose Fermentation   The SSF process combines the enzymatic hydrolysis and fermentation processes into a single operation. In this process, the yeast converts the sugars to ethanol as soon as they are produced, thus preventing the build-up of sugars which inhibit the activity of the enzymes, and thereby reducing the amount of expensive enzymes which are required. The reaction time is somewhat longer than in the previous case because the introduction of yeast into the hydrolysis process requires that the reaction be run at a lower temperature. The second major innovation is the addition of a xylose

fermentation step, which uses a genetically engineered *E. coli* to ferment the xylose to ethanol. This process is now under development in the United States at the National Renewable Energy Laboratory (NREL). All of the major steps have been demonstrated individually, but integrated operation has not yet been reported. This laboratory scale analysis is based on a study of the NREL process by Chem Systems (1990), and the advanced case on an NREL analysis by Hinman *et al.* 1991.

The laboratory scale SSF-xylose fermentation process results in decreased capital investment, due primarily to the reduced enzyme requirements. The investment per unit of production is further reduced because of the increased yield provided by the incorporation of a xylose fermentation process. The laboratory-scale technology converts biomass to ethanol with an efficiency of 39%. The resulting cost of production is $17.3/GJ or $0.37/liter.

The overall process for the advanced SSF-xylose fermentation case is identical to the laboratory-scale process. However, in this case the process yields are increased (overall yield based on six-carbon sugars is increased from 72% to 90%), and the xylose fermentation efficiency is increase from 90% to 95%. Also, the time required for the various biological processes are decreased by a factor of two or more. These improvements have not yet been achieved. However, they are representative of what might be achieved with further research and development.

The advanced SSF - xylose fermentation case has a biomass to ethanol efficiency of 53%, and a reduced capital investment. This efficiency approaches the theoretical limit imposed by the composition of the biomass. The projected cost of production is $12.5/GJ or $0.26/liter.

Thermochemical Conversion of Biomass to Methanol The production of methanol from biomass consists of four major processes: 1) gasification of the biomass to produce raw synthesis gas (a mixture of carbon monoxide, hydrogen, carbon dioxide, and water), 2) increasing the H_2/CO ratio to that necessary for methanol synthesis, 3) removal of excess carbon dioxide, and 4) conversion of the carbon monoxide and hydrogen to methanol (Figure 2).

In the gasification process, heat produced by the oxidation of a portion of the biomass

$$C + O_2 \rightarrow CO_2$$
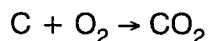
is used to drive the endothermic gasification reactions:

$$C + H_2O \rightarrow CO + H_2$$

$$C + CO_2 \rightarrow 2\ CO$$
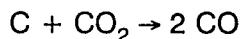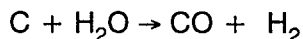
The heat may be supplied by supplying oxygen to the gasifier and carrying out the partial oxidation of the biomass in the gasifier itself, or biomass, syngas or char may be burned in a separate combustor and the heat transferred to the bed

either through a heat exchanger or a stream of circulating solids. If the partial oxidation is carried out in the gasifier, pure oxygen must be used to minimize the cost of compressing the syngas to the pressure required for methanol synthesis, and to minimize the amount of gas which must be purged to prevent a build-up of inerts in the methanol synthesis process.

The syngas produced in the gasifier has a H_2/CO ratio less than the 2.0 required for methanol synthesis. The H_2/CO ratio is increased in some cases by reforming any methane or hydrocarbons present:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
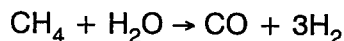
and by running the water gas shift reaction, which trades CO for additional H_2:

$$CO + H_2O \rightarrow CO_2 + H_2$$
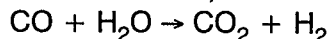
The excess CO_2 and any sulfur containing acid gases are then removed with aqueous potassium carbonate, and the resulting gases are sent to the methanol synthesis process, where the CO and H_2 are combined to produce methanol:

$$CO + 2 H_2 \rightarrow CH_3OH$$
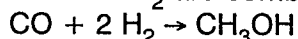
Because the per pass conversion of syngas to methanol is equilibrium limited, a recycle process is used, where the methanol is separated from the product gases, and the unconverted syngas is returned to the reactor. The methanol is then purified by distillation.

The major advantage of the thermochemical conversion processes is that they use very high temperatures (approximately 1,000°C) to break down the biomass to simple molecules such as CO, CO_2, H_2 and H_2O. Therefore, thermochemical conversion processes are relatively unaffected by the detailed structure of the biomass, and are capable of using the entire feedstock (cellulose, hemicellulose and lignin). The disadvantage of the thermochemical processes is that the practical efficiency of the individual conversion steps is lower. The generation of the raw syngas requires the input of heat at roughly 1,000°C to drive the gasification reactions.

Biomass

Gasification

Shift/ Reforming

CO2 Removal → CO2

Methanol Synthesis
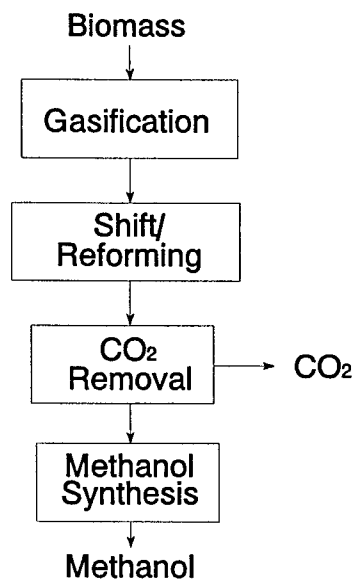
Methanol

Figure 2   Thermochemical conversion of biomass to methanol.

Conversely, the methanol synthesis step produces large amounts of heat, but at a much lower temperature (230-300°C). Because of the temperature mismatch, the heat given off in the synthesis process cannot be used to drive gasification. Thus, because biomass must be burned (either in the gasifier or in a separate combustor) to drive the highly endothermic gasification reactions, the theoretical maximum biomass to methanol conversion efficiency is on the order of 52-58%, depending on the details of the process.

The four cases we analyzed were: 1) Koppers-Totzek (K-T) gasification with low-pressure methanol synthesis (commercial), 2) Institute of Gas Technology (IGT) gasification with liquid phase methanol synthesis (pilot scale), 3) Battelle-Columbus (BCL) gasification with low- pressure methanol synthesis (advanced, base-case), and 4) the BCL gasification low- pressure methanol synthesis process with hot gas clean up (advanced conceptual). The processes are summarized below. The operating characteristics are shown in Table 4, the capital investment in Table 5, and the cost of production summaries are presented in Table 6.

Table 4   Characteristics of the biomass to methanol processes.

[handwritten annotations in margin and around table:]

feed rate = 1818 tonne/day @ $46/dry tonne   3636 tonne/day @ 50% moisture

meoH = 6.63 lb/gal

$(6.63 lb/gal)(\frac{tonne}{2205 lb}) = \frac{1 tonne}{332.5 gal}$

dry to 5-15% moisture content

Technology	Koppers Totzek (Commercial)	Institute of Gas Technology (Pilot)	Battelle-Columbus (Base Case)	Battelle-Columbus (Advanced Case)
Gasifier Type	Direct	Direct	Indirect	Indirect
Heating Mechanism	Partial Oxidation	Partial Oxidation	Circulating Heated Sand	Circulating Heated Sand
Gasification medium	Oxygen-steam	Oxygen-steam	Steam	Steam
Temperature (°K)	1255	1255 *(1800°F)*	1049	1049 *(1429°F)*
Pressure (atm)	1	25 *(368 psia)*	1	1
Cold Gas Yield (corrected for CH₄ shift) m³/tonne	1360	1485	1510	1510
Methanol Synthesis Technology	*(Lurgi/ICI)* Low-pressure	Liquid-Phase	Low-pressure	Low-pressure
Overall biomass to fuel energy efficiency (%)*	40.3	45.4	53.5	53.5
Annual production liters/yr gallons/yr GJ/yr	329 E6 87 E6 5.2 E6	384 E6 102 E6 6.1 E6	469 E6 124 E6 7.4 E6	469 E6 124 E6 7.4 E6

*   The efficiency cannot be directly calculated from the feedstock consumption and the annual methanol production because the process is a significant consumer of imported electricity.

[handwritten at bottom:]

tonne/yr $2,61 \times 10^5$ $3,07 \times 10^5$ $3,73 \times 10^5$ $3,73 \times 10^5$

tonne/day   717   840   1021   1021

$\frac{tonne feed}{tonne meoH}$ 2,54   2,16   1,78   1,78

xxi

Table 5 Capital investments for the thermochemical conversion of lignocellulose to methanol. (1990 costs)

Technology	Koppers Totzek (Commercial)	Institute of Gas Technology (Pilot)	Battelle-Columbus (Advanced Base Case)	Battelle-Columbus (Advanced Conceptual Case)
Investment (million $)				
Feedstock Preparation	38.3	17.1	20.3	20.3
Oxygen Plant	49.9	43.3		
Gasification	97.5	29.4	7.9	7.9
Solids Removal		0.8	1.7	12.8
Shift/Reforming	0.8	31.9	41.3	0.03
Acid Gas Clean-up	11.1	11.8	11.6	11.6
Gas Cooling		2.0		
Syngas Compression	10.9	8.2	25.7	25.6
Methanol Synthesis	21.4	24.2	32.2	32.2
Utilities, Offsites	57.4	42.2	35.2	27.6
Land, Owners costs, fees, profit, start-up cost	37.3	29.7	23.2	20.0
Total Cost	**324.6**	**240.6**	**199.2**	**158.2**
Cost/Unit of annual production ($/GJ-yr)	**62.4**	**39.1**	**26.5**	**20.8**

Commercial Scale Technology - Koppers Totzek Gasification - Low Pressure Methanol Synthesis The commercially available Koppers-Totzek gasifier was originally developed for use with coal, and approximately 50 have been built worldwide over the past 40 years. Most of these installations use lignite or heavy naphtha as a feedstock. The gasifier has been tested on wood, but there are no commercial integrated wood-to-methanol processes in operation. The gasifier is coupled to a low-pressure methanol synthesis process of the type sold by Lurgi and Imperial Chemical Industries (ICI), which account for over 90% of the world's installed methanol capacity. The analysis of this system is based on a study carried out by Chem Systems (1989) for the United States Department of Energy.

The K-T gasifier is an oxygen-blown, atmospheric pressure, entrained-bed design. Because it uses extremely short residences times, extensive grinding is used to reduce the size of the feedstock, and the biomass must be dried to 5% moisture. Because the heat needed to drive the gasification process is produced by partial oxidation inside the gasifier, an expensive oxygen plant is required. After gasification, the raw syngas is cooled to ambient, and the particulates and tars

Table 6 Cost of production for the thermochemical conversion of biomass to methanol.

Technology	Koppers Totzek (Commercial)	Institute of Gas Technology (Pilot)	Battelle-Columbus (Base Case)	Battelle-Columbus (Advanced Case)
Raw Materials				
Wood	5.72	5.03	4.01	4.01
Chemicals	0.10	0.28		
Utilities				
Electricity	0.40	0.40	1.50	1.10
Steam		-0.19		
Cooling Water	0.01	0.03		
Feedwater	0.01	0.04		
Fuel		0.20		
Other variable costs			0.44	0.44
Labor	0.20	0.15	0.12	0.12
Maintenance	1.52	1.05	0.60	1.03
Overhead	1.50	0.82	0.50	0.60
Insurance, Property taxes	1.14	0.60	0.40	0.31
Total annual operating costs	9.65	8.01	6.54	6.50
Total capital charges (@ 30%)	19.01	12.10	8.30	6.42
Cost of Production $/GJ $/l	**28.50** **0.448**	**20.10** **0.311**	**14.70** **0.231**	**13.10** **0.204**

are removed. The syngas is reheated to run the water gas shift reaction, and the gases are again cooled before they enter the CO_2 removal unit. Finally, the syngas is compressed and sent to methanol synthesis.

While the overall biomass-to-fuel conversion efficiency of this process is quite respectable (40%), the capital investment of $325 million or $62.4/GJ-yr is very large (approximately twice that of the ethanol production processes). This is a result of the very expensive gasifer used, the large drying and grinding costs, the need for an oxygen plant, the need to compress large gas streams to the methanol synthesis temperature, and the multiple heating and cooling cycles to which the gas is subjected. Thus, the cost of production is dominated by the charges related to the capital investment, and feedstock costs play only a minor role in the economics. The cost of production is $28.5/GJ or $0.45/liter.

This process uses the Institute of Gas Technology "Renugas" gasifier, coupled to an Air Products/Chem Systems liquid-phase methanol synthesis process. Both of these processes have been demonstrated individually at the 10 tons/day scale. This portion of the analysis is also based on the Chem Systems (1989) report used in the previous case. The IGT gasifier is a fluidized-bed, partial oxidation unit. As such, it uses larger residence times and can use a wood chip feedstock directly (without excessive and expensive grinding), and does not require an extremely dry feedstock. The gasifer is operated at pressure, and thus the overall compression costs are slightly reduced because feeding pressurized solids into a gasifier requires less energy than compressing the large volumes of gas produced from the solids during gasification. Because the gasifier is run at pressure, the syngas produces a moderate amount of methane, which must be reformed to produce additional CO and H_2. Although this process is expensive, it increases the overall yield. The gases are again subjected to multiple heating and cooling cycles to remove the tars, particulates, and CO_2. The liquid phase methanol synthesis provides better temperature control and slightly better per pass conversion, and has economics which may be slightly superior to the standard low pressure process.

The overall conversion efficiency of the process is increased to 45%, and the capital investment is reduced as well. The cost of production is still dominated by the capital investment ($39/GJ-yr), to which the oxygen plant is a major contributor. The cost of production is reduced to $20.1/GJ or $0.31/liter.

Advanced Systems: Battelle-Columbus Gasifier - Low Pressure Methanol Synthesis
The major improvement in the advanced system is the use of the indirectly heated BCL gasifier, which eliminates the need for the oxygen plant (because the heat is transferred from the combustor to the gasifier by a circulating bed of sand, the combustor can use air instead of oxygen). Because of the indirect design, the BCL gasifier produces large amounts of methane and hydrocarbons, which increases the yield but also requires a large capital investment in the reformer. The remainder of the process is similar to the previous systems.

The increased yield brought about by the reforming of the hydrocarbons increases the conversion efficiency to 53%, approaching the theoretical limit for such processes. Largely because of the elimination of the oxygen plant, the capital cost is also reduced, as is the investment per unit of production ($29/GJ-yr). The cost of production is $14.7/GJ, or $0.23/liter.

The advanced-case system uses the same gasifier and methanol synthesis process, but adds hot gas clean-up technology (developed for use with coal gasifiers) to eliminate much of the repeated heating and cooling of the syngas. By using high temperature particulate and tar removal, the hot raw syngas can be fed directly to the reformer. This not only reduces heat exchange costs, but also eliminates a major steam consumption. (In previous processes the steam in the raw syngas was condensed out when the gases were cooled before the

particulate-removal step, and high pressure steam was then added before the syngas entered the reformer/water-gas shift reactor.)

The advanced case has a reduced capital investment ($18/GJ-yr) and an efficiency identical to the previous BCL-based system. The cost of production in the advanced case is projected to be $13.1/GJ or $0.20/liter.

Comparison of Methanol and Ethanol Production from Biomass The cost of production of methanol and ethanol from biomass is shown on an energy basis in Figure 4. The graphs show quite clearly that the economics are dominated by the capital investment, and secondarily by the feedstock costs. The decreasing costs of the ethanol processes were driven by the improvement in yield from case to case, which both reduced the feedstock cost and spread the capital investment over a larger base of production. The improvements in the methanol cases were brought about by simplifying the process (eliminating expensive processing steps) and only secondarily by improving the yield (which started out relatively high).
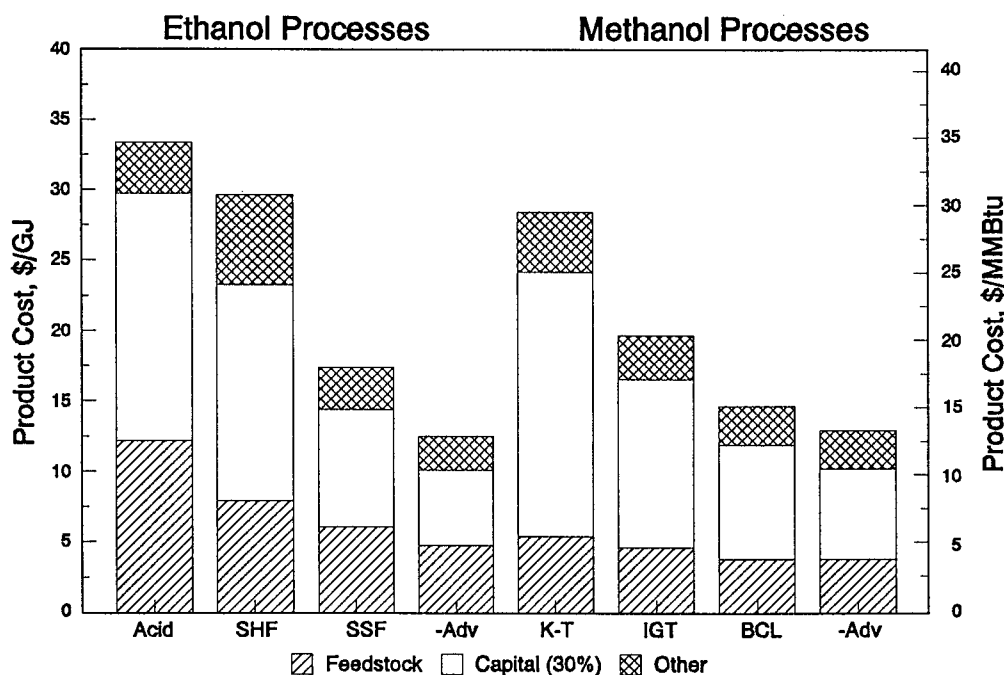
Figure 3   Cost of production breakdown for methanol and ethanol from biomass.

In an overall sense, capital investment per unit of production is similar for the biochemical and thermochemical processes. We see that the investment per unit-of-annual-capacity is similar at all stages of development. There is no fundamental reason for this, it merely suggests that equivalent results can be achieved with slow processes which operate in large vessels at low temperatures and pressures, and rapid processes which require only small vessels but operate at high temperatures and pressures.
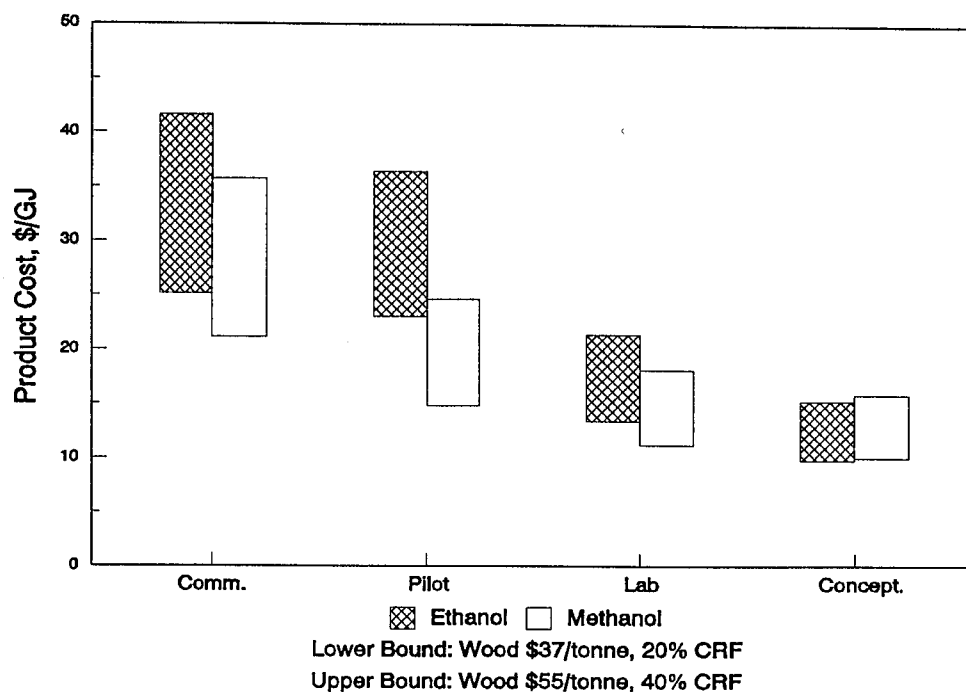
Figure 4 Comparison of the economics of methanol and ethanol from biomass.

When comparing the two types of processes, it is instructive to look not only at the cost of production, but simultaneously at the uncertainty of the estimate. Figure 4 shows the cost of methanol and ethanol with uncertainty bars taken from the previous sensitivity analyses. The important conclusion of the analysis is that for the processes which have been demonstrated at the commercial and pilot scales, methanol production is considerably less expensive than ethanol production. However, for the laboratory scale processes there is little difference, and for the "conceptual" processes which attempt to estimate the limits of process improvement, the economics of the methanol and ethanol production are virtually identical.

This result is a direct outgrowth of the basic nature of the biomass feedstock, and the fundamental characteristics of the two types of processing. The ethanol processes convert the carbohydrate fraction of the biomass (which accounts for roughly 60% of the energy content of the feedstock) to ethanol with an extremely high efficiency (roughly 85%, compared with a theoretical limit of 95%). Thus, the overall efficiency of converting biomass to ethanol is approximately 50%. In contrast, because of the temperature mismatch between the endothermic gasification process (which requires heat at 1,000°C) and the exothermic methanol synthesis process (which produces heat at only 230-300°C), the maximum efficiency of the thermochemical conversion process is only 52-58% (depending on the detailed assumptions). However, because the gasification process operates at high temperatures and converts all fractions of the biomass

to simple molecules such as CO, CO_2, H_2 and H_2O, from which the methanol is synthesized, the methanol synthesis processes can use all fractions of the feedstock, not just the carbohydrate fraction. A thermochemical process which achieves 90% of the theoretically possible 58% efficiency therefore has an overall process efficiency of a little better than 50%. Thus, the ultimate efficiencies of the processes which produce methanol and ethanol from biomass are essentially identical.

Sensitivity analyses were carried out to determine the influence of the major assumptions (plant size, feedstock cost, and capital recovery factor) on the cost of production, and to determine whether changes in any of these assumptions would have affected the conclusions of the study. In general, the economics of ethanol production are more sensitive to changes in feedstock cost, while the more capital intensive thermochemical processes are more sensitive to the assumed capital recovery factor or the size of the plant. However, we found that the conclusions of this study are unchanged over a very wide range of plant scales, feedstock costs, and economic assumptions.

In summary, the economics of near-term thermochemical methanol synthesis processes are superior to those of the near-term biochemical process. This is a direct result of the lower conversion efficiencies of the near-term biochemical processes, due to the inability of the early designs to ferment the five-carbon sugars (xylose) to ethanol. For the advanced cases, the economics of methanol and ethanol are essentially identical, which results from the fact that the limiting conversion efficiencies of the biochemical and thermochemical conversion processes are essentially the same. With equivalent efficiencies and no significant differences in the capital investment, the ultimate economics of both processes are the same.

1   Introduction

The production and use of alcohol fuels from renewable resources has received extensive research and development over the past 15 years. This interest results from concerns over the price and availability of conventional petroleum based fuels, balance of payment problems which result from high oil imports, urban air quality problems created by the combustion of gasoline and diesel fuels, and more recently, concern over the accumulation of carbon dioxide in the atmosphere and its effect on the global climate. The production of alcohol fuels (methanol and ethanol) from renewable resources such as crop and forestry wastes, municipal solid wastes, and dedicated energy crops has the potential to alleviate many of these problems. However, in order for renewable alcohol fuels to make a significant contribution, they must be produced at a competitive cost.

Alcohols can be blended directly with gasoline, converted to ethers to produce a superior blend stock, or burned as neat fuels. In all cases, the differences between the alcohols and hydrocarbon fuels are much greater than the differences among the alcohols themselves. Thus, since neither methanol nor ethanol is vastly superior to the other, and the utilization technology for both fuels is quite similar, the economics and efficiency of the processes for converting biomass to alcohols are quite important.

Although numerous reports evaluate individual processes for the production of methanol and ethanol from biomass, it remains difficult to compare the status of these two technologies. Most of the studies focus on a single conversion process and use different economic assumptions, different sized plants, and different feedstocks. Even more importantly, it is necessary to evaluate the differing degrees of optimism and pessimism the different authors bring to their studies. Finally, it is dangerous to compare processes which are in different stages of development. Unfortunately, the lack of a consistent comparison of the various processes makes it difficult to rationally plan national research programs.

1.1   Study Methodology

The objective of this study is to compare technologies for the production of methanol and ethanol from biomass on a consistent basis. The processes are compared at four different levels of development, technology which has been 1) commercially demonstrated 2) demonstrated at the pilot-scale and 3) demonstrated at the laboratory scale, and 4) advanced cases which attempt to predict the potential for improvement (conceptual technology). The study was built on performance and cost data contained in existing published reports, adjusting capital, feedstock, and economic parameters to a common basis.

There is extensive literature representing millions of dollars of engineering effort on the engineering analysis of processes for producing alcohols from biomass. These studies provided the raw data for this study. One obvious reason for this approach was cost; a study which built up process designs for each of the

processes would cost many times as much as was available for this project. Equally important, these studies represent a significant investment of expertise and were carried out by the groups which were most familiar with the processes. The primary problem in basing an overall study on such data is not the technical content of the studies (the studies selected to provide the data for this comparison are of extremely high quality), but that they use different bases and evaluate processes at different stages of development and are therefore not directly comparable.

The most important step in comparing technologies is to only compare processes which are at similar stages of development. Merrow (1981) compared cost estimates for a variety of new processes to the ultimate cost of the first plant as a function of the level of process definition or knowledge (laboratory data, integrated laboratory experiments, integrated pilot-plant data). Universally, the estimated cost grew as the level of definition improved. By far the most important steps in creating an accurate cost estimate were running a process from start to finish (even at the laboratory scale), and running an integrated pilot plant. Contrary to popular belief, private industry was no more accurate than the government in its estimates. Thus, to avoid comparing current technology with optimistic projections, we will compare the technologies at three different levels of development: commercial practice, integrated pilot plant, and projections based on theoretical and laboratory data.

A second means of improving comparability was to base our comparison only on studies where detailed cost estimates were made directly from process material and energy balances. This insured that all of the analyses incorporated a similar degree of thoroughness.

Once the studies were selected, it was necessary to adjust the results to a common basis. This involves selection of a common plant size, feedstock composition and cost, consistent assumptions for calculating the total capital investment from the equipment cost, and common economic assumptions for calculating the cost of production. The detailed assumptions used in this comparison are described in Section 3.

1.2   Intended Uses of the Results

In a study such as this, it is useful to understand the overall accuracy of the results, as well as how this affects the use of the results. With the partial exception of the commercial technology cases, none of the processes described in this report have been run from start to finish in an integrated manner. Many of the calculations used to prepare the mass and energy balances were based on assumed efficiencies and equipment performances. Further, the factored cost estimating methodologies used in calculating the capital investment have an accuracy of only $\pm 30\%$.

The actual uncertainty in the projected cost of production is the sum of the uncertainty in the cost estimating methodology and the uncertainty inherent in the

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flow sheet itself. Because most of the processes described in this report have never been run from start to finish in an integrated manner, there is a significant possibility that the process would not necessarily perform exactly as described in the process flow sheet and material balance. This technical uncertainty is probably at least as important as the cost estimating uncertainty. (Because a large part of the uncertainty in the calculated cost of production is a direct result of the uncertainty in the process performance, the cost estimates presented in this report are probably as accurate as can be achieved at this time. Significant improvements in accuracy will require further research and process development.)

A third set of uncertainties comes from our imperfect knowledge of the costs of the feedstocks, and the value of the fuels which we produce. For example, except for the supply of wood chips to the pulp and paper industry, there is no actual large-scale experience on which to base feedstock cost estimates. Also, although ultimate usefulness of any of the production processes depends on whether they can produce alcohol fuels at a price which is competitive with conventional petroleum fuels, the record of energy analysts' forecasts of market prices for petroleum and natural gas is abysmal.

A final set of uncertainties arises from the choice of conditions under which we compare the processes. For example, the process economics are sensitive to the plant size, feedstock cost, and economic assumptions. Because each of the processes will have a different sensitivity to these parameters, the choice of the conditions under which the processes are evaluated could affect the conclusions. Therefore, we carried out sensitivity analyses to be sure that our conclusions were valid over a wide range of assumptions.

In light of these uncertainties, we can identify the uses and limitations of the results. The studies of the different processes for producing methanol and ethanol from biomass have overlapping individual and institutional authorship and share many common data sources. Further, even though the individual estimates have a high uncertainty, they share many common assumptions. Thus, while the absolute selling prices may not be accurate, many of the inaccuracies will not affect the relative costs of the different processes. This means that this study quite accurately portrays the degree of improvement from commercial to pilot to laboratory and conceptual technology. The comparisons between ethanol and methanol production technology at a similar stage of development are also relatively accurate, but less so than the comparisons between similar technologies at different stages of development. The main reason for this is the difficulty in choosing examples of ethanol and methanol production processes which are truly at similar stages of development.

A second value of the study is that since all of the economic results were derived using a consistent methodology, any differences in the selling price of the alcohols are directly traceable to the technical assumptions. Thus, excellent conclusions can be reached concerning the relative importance of the various

process parameters, and the areas in which research attention should be focused.

The predictions of absolute selling prices for methanol and ethanol are much less certain. As was shown above, the uncertainty in the estimating procedure alone is ±30%. The actual uncertainty is the sum of the estimating uncertainty and the equal or larger uncertainties in the assumed performance. Further, the estimated costs are for a mature technology, not a first-of-a-kind plant (which would certainly have much higher production costs). Thus, comparisons of the predicted selling price of the methanol and ethanol with current or projected fossil fuel prices are uncertain at best, and have the potential to be quite misleading.

2   Overview of Feedstock Production, Conversion, and Utilization Technologies

This section provides a brief overview of the technologies and issues important in growing the lignocellulosic feedstock, converting it to ethanol or methanol, and burning the alcohols in an internal combustion engine. The purpose of this section is not to provide a detailed review of any of these areas (especially since feedstock production and fuel utilization are well outside the scope of this report), but merely to allow the reader to easily fit the detailed descriptions which follow into an overall framework.

2.1   Feedstocks

Through the process of photosynthesis, plants convert water and carbon dioxide into carbohydrates. In photosynthesis, the energy of sunlight is converted into chemical bond energy with an efficiency which can be as high as 7% under ideal conditions, but which is generally much lower. Thus, plants store the sun's energy in a solid form which can be readily converted to liquid transportation fuels.

In sugar cane, up to 20-30% of the captured chemical energy can be in the form of simple sugars which are readily fermentable to ethanol. In grains such as corn or wheat, much of the energy is stored as starch which is also easily fermented. In woody biomass or grasses, the energy is converted into the structural carbohydrates such as cellulose and hemicellulose (which can be converted to fermentable sugars), and into lignin (which is a non-fermentable phenolic polymer). The lignocellulosic materials are, in general, less expensive than the sugar or starch crops because they have no food value and cost less to produce. Of course, all of the fractions of these feedstocks are useable by thermochemical processes which use extreme heat to break the complex biopolymers into simple gases or hydrocarbons.

The interactions between feedstock composition and the conversion processes are discussed in detail in sections 5 and 6.

2.2   Conversion Processes

Lignocellulosic materials can be either biochemically converted to ethanol or thermochemically converted to methanol. The following sections provide a very brief overview of these technologies (which are described in detail in Sections 5 and 6).

2.2.1   Ethanol Production by Biochemical Processes

Man has known how to produce ethanol for at least 8,000 years. The ability of yeast to produce alcohol (ethanol or C_2H_5OH) was known to the Sumerians and Babylonians before 6000 B.C. The discovery of distillation to concentrate alcohol

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is credited to the Chinese, and by the 14th century, distilled spirits were common in many parts of the world.

In the absence of air, yeast converts sugar into ethanol and carbon dioxide. Ethanol can be made from a number of renewable feedstocks, including sugar crops such as sugar cane, starch crops such as corn, and lignocellulosic materials such as grasses and trees. The easiest of these to process are the sugar crops. For example, in making fuel ethanol from cane sugar, the sugar cane (containing 20-30% sugar) is chopped into short pieces and crushed. The sugar is then easily washed from the cane with hot water, fermented by yeast to produce a 10% ethanol stream, and concentrated by distillation. Brazil currently makes 11 billion liters/year of ethanol from sugar cane.

In the more-tropical countries, most fermentation ethanol is made from corn or other grains, which contain roughly 80% starch, a polymer of glucose. Enzymes hydrolyze (break down) the starch chains into individual sugar molecules that are then fermented in the conventional fashion to produce ethanol. The current annual United States production of fuel ethanol is about 3 billion liters (Sinor 1990).

The cost of ethanol production from sugar and starch-bearing crops is dominated by the cost of the feedstock. Therefore, much research has been carried out on the conversion of less expensive and more plentiful lignocellulosic materials. In these processes, acids or enzymes are first used to break down the cellulose into glucose, and the hemicellulose into a mixture of sugars such as glucose, xylose, galactose, arabinose and mannose. These sugars are then fermented to produce ethanol.

Biological processing offers a number of advantages. First, the enzymes and micro-organisms used in the bioprocessing of the materials typically catalyze only one reaction, minimizing the formation of unwanted byproducts. Bioprocesses are also extremely efficient. For example, the conversion of glucose to ethanol can have an efficiency of greater than 95%. Additionally, biological processes can be carried out at near ambient pressures and temperatures, so that the cost of the equipment is modest. Finally, biotechnology and bioprocessing are relatively new areas, and there is considerable room for process improvement.

These attributes also result in a number of disadvantages. The same tendencies towards selectivity which minimize by-product production, also increases process complexity. For example, the yeasts typically used to ferment glucose to ethanol are incapable of fermenting xylose (the second most prevalent sugar in biomass). Thus, additional fermentation organisms have had to be developed. Similarly, although biological processes can be extremely efficient at converting sugars to alcohols, they are totally incapable of fermenting the lignin fraction (which can account for over 30% of the total energy content of the feedstock). Finally, because biochemical processes are carried out at low temperature, they are relatively slow and require hours or days to reach completion.

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2.2.2 Methanol Production by Thermochemical Processes

Methanol, also known as wood alcohol, was discovered by Robert Boyle in 1661 and was first synthesized by Berthelot in the 1850s. From 1830 to 1923 wood alcohol was obtained by the high-temperature destructive distillation (pyrolysis) of wood. In 1913, Mittasch and his associates at BASF successfully produced methanol and other oxygenated compounds from carbon monoxide and hydrogen using iron-oxide catalysts. The crucial step leading to the large-scale industrial synthesis of methanol was the development of sulfur-resistant zinc oxide-chromium oxide catalysts. By the end of 1923, a large-scale process producing methanol from carbon monoxide and hydrogen was in place at BASF.

The major process improvement since then has been the reduction in operating pressures and temperatures brought about by ICI's introduction of low pressure copper oxide catalysts. Methanol is now one of the largest volume chemicals, with a worldwide production capacity of 21 million tonne/year. Of this, roughly 85% is used in the chemical industry as a solvent or as the starting material for additional synthesis, and 15% is used as a fuel (Fiedler et al. 1990).

Methanol can be produced from virtually any carbon source, including fossil-fuels such as natural gas, petroleum fractions (such as naphthas), and coal, and from biomass resources such as woody or herbaceous plants. Currently, virtually all methanol is produced from natural gas and naphtha. Methanol is produced by high-temperature thermochemical processes which have very high rates and are capable of using all fractions of the feedstock.

Methanol production consists of three major processes: 1) generation of synthesis gas (syngas), 2) syngas upgrading, and 3) methanol synthesis and purification. When natural gas or naphtha are used as feedstocks, high- temperature steam reforming is used to produce the CO and H_2 needed for methanol synthesis. When coal or biomass is the feedstock, the solid feed is gasified to produce the syngas. For natural gas and naphtha feedstocks, gas upgrading primarily consists of removing CO_2 from a clean gas stream. For coal and biomass feedstocks, the primary synthesis gas is first reformed or shifted to produce a syngas with a low methane content and a proper H_2/CO ratio, and CO_2 and sulfur compounds are removed to protect the methanol synthesis catalyst. In the methanol production step, a copper-zinc oxide catalyst is used to react the CO, H_2, and a small amount of CO_2 to form methanol. Reaction conditions are 230-300°C and 50-100 atmospheres.

The major advantage of the thermochemical process is that since it first converts all of the feedstock to small molecules (such as CO, H_2, CH_4, CO_2 and H_2O), then builds the methanol (CH_3OH) from these simple building-blocks, the process is able to use virtually any carbon source, and can easily convert all fractions of the biomass (cellulose, hemicellulose, and lignin) to methanol. A second advantage is that since the process is carried out at high-temperature, the actual reactions are carried to completion in seconds or minutes.

However, these characteristics bring a number of disadvantages as well. Although the thermochemical processes can work on a much larger fraction of the feedstock than can the biochemical processes, the practical efficiency of the individual conversion steps is much lower. While the gasification step requires heat and the methanol synthesis step produces heat, the gasification is carried out at a much higher temperature and cannot use the heat produced during methanol synthesis. Thus, the overall process has an efficiency of only 40-60%. Also, although the conversion processes are carried out quite rapidly, high operating pressures and temperatures lead to the use of expensive equipment.

2.3   Alcohols as Fuels

Alcohols can be blended with gasoline, reacted with isobutylene to produce high-value ether-blend stocks, or used directly as neat fuels. In this section, we first compare the physical and chemical properties of the alcohols, ethers, and gasoline. Then, the issues surrounding their use are described. A recent review is provided by Black (1991).

2.3.1   Physical and Chemical Properties of the Alcohols, Ethers, and Gasoline

The physical and chemical properties of the alcohols (methanol and ethanol), their ether derivatives (MTBE and ETBE), and gasoline are summarized in Table 1.31. The most prominent difference is that as oxidized species, the alcohols and ethers have a lower heating value than do hydrocarbon fuels. The reduction in heating value is most severe for the highly oxygenated alcohols; the lower heating values of methanol and ethanol are 50% and 66% that of gasoline, respectively. The reduction is relatively small for the ethers (MTBE and ETBE) which have a lower oxygen content. The alcohols are small, compact, relatively symmetrical molecules, and have very high-octane numbers, which allows the use of higher compression ratios and more efficient engine operation when alcohols are used as fuels. The ethers share this high octane characteristic. The alcohols and ethers are also excellent octane enhancers, and are frequently added to gasoline to improve its octane. As polar compounds, the alcohols have much higher heats of vaporization than do the ethers or gasoline, which is advantageous as it decreases the work of compression and increases engine efficiency. Also, the vapor pressure of the alcohols and ethers is much lower than that of gasoline, which decreases evaporative emissions, but in the case of neat alcohols, makes the engines much harder to start. The most important point to be gained from this overview of physical and chemical properties is that we can think in terms of three categories of fuels, alcohols, ethers, and hydrocarbons (gasoline). There are substantial differences between the three categories, with each having its own set of advantages and disadvantages. However, the variation within the categories is relatively small. That is, the properties of methanol and ethanol are quite similar to each other, as are the properties of MTBE and ETBE. As we will see further in the next section, the differences between the alcohols is small enough that the acceptance of the fuels will largely be determined by fuel

price and availability, not by the relative advantages in use of methanol *vs.* ethanol, or MTBE *vs.* ETBE.

2.3.2 Alcohol/Gasoline Blends

Low level blends of ethanol and methanol with gasoline can be burned in unmodified automobile engines. Alcohol blends can cause engines to run lean, thereby reducing carbon monoxide emissions. The effect is most pronounced in colder climates, and in older vehicles without adaptive feedback or controls.

Table 2.1 Properties of methanol, ethanol, ethers, and gasoline.

Property	Methanol	Ethanol	MTBE	ETBE	Isooctane	Unleaded Regular Gasoline
Formula	CH_3OH	C_2H_5OH	$(CH_3)_3COCH_3$	$(CH_3)_3COC_2H_5$	C_8H_{18}	C_4 TO C_{12}
Molecular Weight	32.04	46.07	88.15	102.18	114	
Density, kg/m³ @ 298 K	790	790	740	750	690	720-780
Air/Fuel Stoichiometric Ratio Mole Basis Mass Basis	7.14 6.48	14.29 9.02	35.71 11.69	42.86 12.10	59.5 15.1	
Lower Heating Value, kJ/kg	19,919	26,780	35,270	36,031	44,420	41,800-44,000
Lower Heating Value, kJ/L	15,736	21,156	26,100	27,023	30,650	31,350-33,000
Octane Numbers						
RON	106	106		118	100	91-93
MON	92	89		102	100	82-84
(RON + MON)/2	99	98		110	100	88
Blending RON	135	114-141[a]	118	117-120[b]		
Blending MON	105	86-97[a]	101	101-104[b]		
(BLENDING RON+MON)/2	120	115	110	111	111	
Atmospheric Boiling Pt. K	337.8	351.6	328.6	344.8		
Vaporization Heat, kJ/kg	1104	839	337		406	
Flash Pt., K	280	285	245			
Ignition Pt., K	737	697	733			
Reid Vapor Pressure, kPa Pure Component Blending	214+	15.85 82.7-186	55.1	30.3 20.7-34.5		55.1-103.4
Water Solubility, weight % Fuel in water Water in fuel	100 100	100 100	4.3 1.4	2 0.6	negligible negligible	negligible negligible

[a] 10% blends
[b] assumed 12.7 blend

Alcohols have high blending octane numbers, and are often used as octane enhancers. The lower energy content of the blends also decreases mileage, but only by a very small amount. The addition of a polar compound such as alcohol to gasoline increases the vapor pressure of the mixture, which leads to increased evaporative emissions of hydrocarbons. The addition of 10% ethanol to gasoline increases the Reid vapor pressure of the gasoline by about 3.4 kPa, while the addition of methanol at a similar level would increase the vapor pressure by 10 kPa.

Because of the large vapor pressure enhancement, methanol blends are not widely used in the United States. However, blends of 3% methanol with a co-solvent are widely used in Europe. In 1988, worldwide use of methanol as a gasoline additive was approximately 190 million liters (Veralin 1989). In the United States, roughly 8% of the gasoline sold was a blend of 10% ethanol in gasoline (3,040 million liters of ethanol).

Modeling studies on the effect of blends on smog formation have lead to contradictory conclusions. Further, as the addition of alcohols leads to increases in some emissions and decreases in others, the effect of alcohol blends on air quality is very dependent on location and time of year (Black 1991, Most 1989, Yaccarino 1989, Gallagher et al. 1990).

2.3.3   Alcohol-Derived Ethers as Blends

Because they are polar compounds and have a lower heating value than gasoline, alcohols cannot be handled like conventional gasoline in common pipelines and tanks, and cannot be easily exchanged. This has severely limited the penetration of alcohol blends, even in situations where the use of blends would appear to be economic (Ludlow 1989).

To eliminate the handling problems and the vapor pressure enhancement caused by the addition of a polar molecule to gasoline, processes have been developed to convert alcohols to ethers. Either methanol or ethanol can be reacted with isobutylene to form methyl tertiary butyl ether (MTBE) or ethyl tertiary butyl ether (ETBE). Like their parent alcohols, they have high blending octane numbers and reduce carbon monoxide emissions (although greater quantities of ethers are required to reach a given oxygen content in the fuel). However, they are not polar and can be handled like conventional petroleum products, shipped though existing pipelines, and are readily exchanged and swapped (Anderson 1989).

Because the ethers are fungible with gasoline, they have been rapidly adopted by the refining industry. The 1991 worldwide MTBE production was 12,765 million liters, and is expected to grow to 1,150,000 million liters by the year 2000 (Zichichi 1991). Approximately 22% of the gasoline sold in the United States in 1988 contained MTBE. While ETBE is not yet in commercial use, the production processes and properties of MTBE and ETBE are similar, and interest in ETBE is increasing (Anderson 1989, Shiblom et al. 1990).

2.3.4 Alcohols as Neat Fuels

Ethanol and methanol can be used as neat fuels in engines which have been appropriately modified. Neat alcohols have several advantages. Engines which burn neat alcohols can have higher efficiencies than do gasoline engines because of alcohols higher octane values (which allow the use of higher compression ratios), higher heat of vaporization (which reduce the work of compression), and lower flame temperatures (which reduce heat loss to the cylinder walls). In general, engines that are optimized for use on alcohols are projected to have efficiencies that are 7-18% greater than a similar, gasoline-fueled engine (USEPA 1989, 1990).

The modifications necessary for gasoline engines to burn alcohols include: new materials of construction in the fuel system, redesigned fuel pumps, higher volume fuel injectors, and the addition of a system to facilitate cold weather starting. Also, higher compression ratios are usually used to take advantage of the alcohols higher octane ratings, and the engine operation is re-optimized. Perhaps the most obvious disadvantage for alcohol fueled vehicles is that the lower energy content of the alcohols implies either a reduction in vehicle range, or an increase in the size of the gas tank (DeLuchi 1988, Black 1991).

A major impetus for the use of alcohol-fueled vehicles has been their potential for air quality improvement. In general, carbon monoxide emissions from alcohol vehicles are similar to those of gasoline vehicles. While NO_x emissions from alcohol fueled engines are lower than those from gasoline-fueled engines, the higher compression ratios likely to be used in alcohol-fueled engines will probably reduce or eliminate this advantage.

Most of the attention has been focused on the effect of alcohols on the quantity and reactivity of the unburned hydrocarbon emissions. In general, evaporative emissions from alcohol fueled vehicles are lower than those from gasoline vehicles due to the lower volatility of the alcohols. Of the unburned fuels that are emitted, the alcohols have a much lower photochemical reactivity than the hydrocarbons. However, the partial combustion products of the alcohols (aldehydes) are quite reactive. In general, when the various effects are accounted for, the alcohols are expected to contribute less to the formation of ozone and smog than will gasoline, although more recent modeling studies show less improvement than did earlier studies (DeLuchi 1988, Harris 1988, Sperling 1988, Black 1991), and show that ethanol may not produce as much of an improvement in ozone levels as does methanol (Carter 1990).

2.4 Alcohol Fuels and the Greenhouse Effect

In an idealized system, the carbon dioxide released during the conversion of biomass to alcohols would be exactly balanced by the photosynthetic carbon dioxide uptake during the growth of the biomass feedstock. In this scenario,

we would have a completely cyclic process, with no net production of greenhouse gasses. In reality, energy inputs are required at several points to drive the cycle. The degree to which the cycle approaches the ideal depends on the amount of fossil inputs used in the harvesting, conversion and utilization processes, and on the efficiency of the conversion and utilization processes (Amann 1990).

Although a number of authors have attempted to estimate the effect of biomass-derived fuels on greenhouse emissions, there is little agreement on either the assumptions or the results. Lynd et al. (1991) estimated that for an efficient lignocellulosic biomass to ethanol conversion process (such as the conceptual case described in this report), the greenhouse emissions per unit of energy delivered to the user would be roughly one fifth of those typical of gasoline. In contrast, DeLuchi (1991) estimates that for the production of ethanol from corn (with significant fossil energy inputs for the production of fertilizer and harvesting, and the use of coal to provide process heat for the conversion), greenhouse emissions would be 24% greater than for simple gasoline usage, but that there would be significant reductions in CO_2 emissions if the conversion process were driven by biomass combustion. In the same study, DeLuchi estimated that the effect of producing methanol from biomass would be to reduce the emissions of greenhouse gases by 56%, compared with the use of gasoline.

Clearly, although the results are quite sensitive to the assumptions regarding fossil fuel inputs and conversion process efficiency, the conversion of biomass to alcohol fuels has the potential to reduce greenhouse emissions, if carried out efficiently.

3 Technical and Economic Assumptions

3.1 Criteria for Comparison

The ultimate objective of the processes analyzed in this report is to produce a fuel alcohol (for use as either a blendstock, a feedstock for the production of ethers or as a neat fuel). Although various proponents have argued for the superiority of either ethanol- or methanol-based fuels, their arguments are generally difficult to quantify. Therefore, since the operational differences between ethanol and methanol are small compared to the differences between alcohols and gasoline, and because the differences between MTBE and ETBE are even smaller, we decided that the figure of merit used to compare processes would be the production cost of the neat alcohol fuel, expressed in terms of United States dollars/gigajoule ($/GJ). (Direct comparison of costs on a basis of $/liter or $/gallon would be misleading, as methanol has a lower heating value of 15,765 kJ/l, while ethanol and gasoline have lower heating values of 21,091 kJ/l, and 32,000 kJ/l respectively).

3.2 Feedstocks

The feedstock was assumed to be a typical hardwood, Red Oak (*Quercus rubra*). The feedstock is delivered to the plant with a moisture content of 50%, at a cost of $46.2/metric tonne (dry basis). The heating value and chemical composition of the feedstock are shown in Table 2.31. Actual feedstock costs will be a function of plant size, and will vary dramatically from site to site, and from year to year at a given site. However, while a rigorous analysis of the cost of feedstock is well beyond the scope of this study, the assumed feedstock cost is consistent with the experience of the pulp and paper industry, and with cost projections for dedicated energy plantations.

This assumption is also consistent with the studies on which this report is based. Equally important, as will be shown in Sections 5 and 6, the choice of a different feedstock or feedstock cost has little effect on the conclusions.

3.3 Plant Size and Design Philosophy

The plants are sized to process 1818 dry tonne/day (2,000 United States tons/day) of dry wood (3,636 tonne/day as delivered at 50% moisture). This plant size is typical of a very large pulp mill, and therefore does not represent an unusual feedstock gathering or materials handling problem. Again, although changes in plant size have a marked effect on the process economics of both ethanol and methanol production, plant scale does not have a large effect on the relative economics of the two technologies.

Depending on the case studied, the plants are either net consumers or net producers of electricity. It was assumed that fractions of the feedstock which were not converted to the product alcohol were burned, if practical. The heat

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Table 3.1 Composition and energy content of a typical hardwood (Red Oak, *Quercus rubra*). Source: Domalski and Milne, 1987.

Component	Weight (%, dry basis)	Gross heat of combustion (kJ/kg)	Fraction of total energy content (%)
Cellulose	46%	17,350	42.3%
Hemicellulose	29.6%	16,676	26.2%
Lignin	24.0%	24,702	31.5%
Total		18,844	

from the boiler was used to raise high-pressure process steam. If the plant required high-pressure steam, this demand was met with the on-site generated steam. After the plant demand for high-pressure steam was met, the remaining steam was expanded to medium pressure in an extraction turbine, generating electricity and lower pressure steam. This steam was used to meet the remaining plant needs. If excess steam was still available, it was expanded to atmospheric pressure to produce additional electricity. In some cases the plant is a net exporter of electricity, and in some cases additional electricity is purchased. For all cases studied, the plants were designed to meet applicable United States air and water pollution regulations.

3.4 Capital Cost Estimation

3.4.1 Time and Place of the Estimate

The capital investment required for a biomass conversion facility is quite site-specific. Most capital cost estimates for chemical process facilities assume that the plant is built on the United States Gulf Coast, an area with skilled construction labor, well-developed infrastructure, and low transportation costs for equipment to the site. However, sites with abundant biomass feedstock supplies are typically in more remote locations, and will have higher capital costs. The capital cost estimate was therefore factored to reflect costs typicalof the United States Midwest, approximately 15% higher than Gulf Coast prices. This factor is roughly appropriate for most typical sites in developed countries. Table 3.2 shows how the capital cost changes as a function of location.

The capital cost estimates were all adjusted to reflect a mid-1990 construction cost. This basis reflects a period of time with relatively "normal," competitive construction costs. These costs are higher than the depressed costs of the early 1980s, but less than might be expected during very robust economic times, or during a crash effort to develop a large, alternative fuels industry.

3.4.2 Estimation Techniques

Capital investment costs have been estimated for a "grassroots plant," a completely new plant erected on a new site. In all cases, the information from detailed process flow sheets, and the material and energy balances were used to estimate the cost of the major pieces of capital equipment. The original studies all used either the Icarus® cost estimating data base, and/or direct quotes from equipment vendors. Icarus® is a very accurate, computer based cost estimating program. From the bare equipment cost, the total installed cost was determined either by a detailed calculation of the parts and labor required (in the case of an Icarus® estimate), or by experience based ratios (in the case where vendor costs were used) (Icarus 1986). By basing cost estimates on Icarus, we significantly reduce the estimating uncertainty due to the accuracy of the equipment cost estimate. As a result, the differences in capital cost are directly attributable to the technical assumptions. To the total installed cost, owners cost, fee, profit and start-up costs were added to arrive at the total plant investment.

Table 3.2 Effect of location on capital cost (U.S. DOE 1989).

Category	Location	Relative Cost
I	U.S. Gulf Coast	1.0
II	U.S. (most lower 48 states) Canada Western Europe Japan	1.15
II / III	Ecuador New Zealand Persian Gulf Venezuela	1.15-1.55
III	Argentina Brazil Chili China Nigeria Thailand	1.55
III / IV	Australia Indonesia Malaysia	1.55-2.25

3.5 Cost of Production Calculations

The cost of production ($/GJ or $/liter) is the total annual cost ($/year) divided by the total annual production of the plant (GJ/year or liter/year). The total annual cost is the sum of the operating charges and the capital charges.

3.5.1 Operating Costs

The production costs include raw materials, utilities, operating costs, and overhead. The primary raw materials cost is that of wood (valued at $46.2/tonne). However, major chemical costs in the ethanol production cases, such as sulfuric acid, lime, ammonia, and nutrients are also calculated directly from the material balance. The most important utility cost is electricity. If electricity is imported to run the plant, it is charged at 4.1¢/kWhr. If excess electricity is produced and exported to the local utility, a credit of 3¢/kWhr is received. Operating costs include the labor needed to operate the plant and the annual maintenance cost (both parts and labor).

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To calculate the labor costs, estimates were made of number of operators and supervisors needed to run the plant. Maintenance, overhead, taxes, and insurance were estimated as fixed fractions of the total capital investment. The major assumptions needed to calculate the operating cost are shown in Table 3.3.

Table 3.3   Basis for operating cost calculations.

Operating factor	91%, 8,000 hr/year
Raw Materials	
Wood	$46.2/tonne
Sulfuric acid	$70.4/tonne
Lime	$30.8/tonne
Ammonia	$99/tonne
Utilities	
Electricity (imported)	4.1 ¢/kWhr
Electricity (exported)	3.0 ¢/kWhr
Water	2.6 ¢/m^3
Labor	
Operators	$29,800/person-year
Foremen	$34,000/person-year
Supervisors	$40,000/person-year
Direct overhead	45% of labor and supervision
General plant overhead	65% of operating costs
Maintenance	3% of total fixed investment
Insurance and property taxes	1.5% of fixed investment

3.5.2   Capital Costs

The contribution of the capital investment to the annual cost is calculated by multiplying the total capital investment by the capital recovery factor (CRF).

The numeric value of the capital recovery factor is a function of many parameters, including the time required for construction, the operating life of the plant, the method used to calculate depreciation, the speed with which the plant is brought up to full capacity, the assumed inflation rate, and most importantly, the internal rate of return (IRR) required by the owner of the plant. Given these values for each of these variables, a single capital recovery factor can be calculated.

Because the cost of production of the alcohol is extremely sensitive to the capital recovery factor, we carried out a sensitivity analysis to show how the CRF varies with the parameters described above (Figure 3.1). We see that the CRF is primarily dependent on the required rate of return (IRR), secondarily dependent on the rate of inflation, and relatively independent of the other assumptions. However, the relative economics of methanol and ethanol production processes were not sensitive to the CRF.

| TDA Base Case | 2 yr constr. | 4 yr constr. | 0% inflation | 5% inflation | Chem Systems |
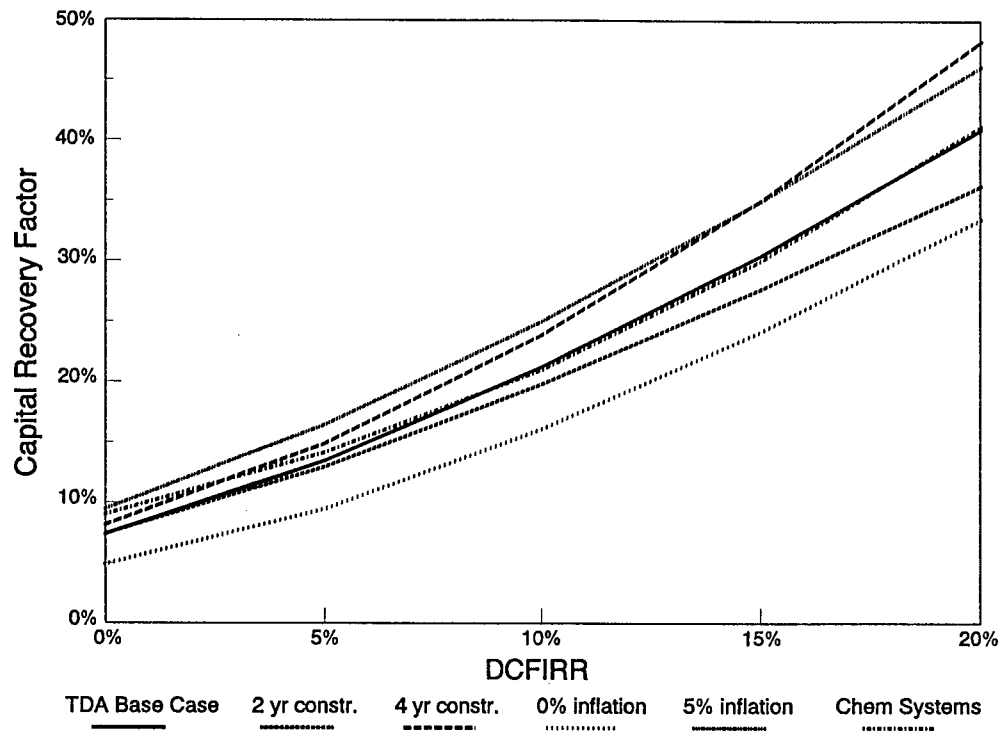
Figure 3.1   Sensitivity of the Capital Recovery Factor (CRF) to the Discounted Cash Flow Internal Rate of Return (DCFIFF) and other assumptions.

Typical rates of return for mature industries range from 12% to 20%, depending upon the economic climate and the philosophy of the company building the plant. Therefore, we assumed a value of 15% for the IRR, and an inflation rate of 3%. This results in a CRF of 30%. The detailed assumptions which went into this calculation are shown in Table 3.4.

Table 3.4   Parameters for the calculation of the Capital Recovery Factor (CRF).

Capital charges of 30% of total capital investment (capital investment × CRF), equivalent to a 15% internal rate of return with the following assumptions:
•   Three-year construction period, 20% of expenditures in year one, 50% in year two, and 30% in year three.
•   20-year life.
•   20-year sum of the digits depreciation.
•   3% inflation
•   30% tax rate

4   Selection of the Cases for Evaluation

The most important step in the analysis is the choice of the processes to be studied. As described above, we were careful to compare processes which are at similar stages of development, and to base our analysis on engineering studies which had used rigorous design and cost estimating methods. The processes to be studied are summarized in Table 4.1, and are briefly described in the following sections.

Table 4.1   Matrix of technologies and engineering studies chosen for detailed evaluation.

	Methanol	Ethanol
Operated at commercial scale	Koppers-Totzek entrained bed gasifier - Lurgi/ICI methanol synthesis (Chem Systems 1989)	Dilute sulfuric acid percolation process (Wright 1986a)
Demonstrated at pilot plant scale	Institute of Gas Technology gasifier - Chem Systems Liquid Phase Methanol Synthesis (Chem Systems 1989)	Iogen enzymatic hydrolysis followed by glucose fermentation (Douglas 1989)
Based on laboratory data and theoretical calculations	Battelle Columbus Gasifier with National Renewable Energy Laboratory (NREL) optimized system design (Bain 1991)	Solar Energy Research Institute Simultaneous Saccharification and Fermentation with fermentation of both xylose and glucose (Chem Systems 1990)
Conceptual design	Battelle Columbus Gasifier with NREL optimized system design "advanced system" (Bain 1991)	NREL simultaneous saccharification process "advanced case" (Hinman et al. 1991)

4.1   Ethanol Production Technology

Commercial Scale Technology - Dilute Acid (Percolation) Technology with Glucose Fermentation

The commercial-scale hydrolysis of biomass has been carried out in Russia using dilute, sulfuric acid-percolation technology. The dilute-acid-hydrolysis process has low yields of sugars from the original lignocellulose, and produces large amounts of degradation products. The overall yield is low because these commercial processes fermented only the six-carbon (glucose) fraction of the biomass to ethanol, but not the five-carbon (xylose) fraction. These processes, and recent improvements to them, were evaluated at the National Renewable Energy Laboratory by the author (Wright and Power 1986a, 1986b).

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Pilot-Scale Technology - Iogen Enzymatic Hydrolysis Process

The Iogen process has been tested at the integrated pilot scale. This process uses a steam explosion pretreatment to break down the lignocellulosic matrix and render it susceptible to enzymatic attack. The cellulase enzymes are produced by highly mutated fungi, and hydrolyze the cellulose to fermentable glucose with high efficiency without the production of by-products. However, because the enzymes are inhibited by the sugars produced during the enzymatic hydrolysis process, the enzymes are used inefficiently, and the ultimate sugar and ethanol concentrations are low. Also, as in the commercial-scale technology, only the glucose is fermented to ethanol, severely limiting the overall process yield. This process was recently analyzed by Douglas (1989) for Energy Mines and Resources, Canada.

Laboratory and Conceptual Systems - National Renewable Energy Laboratory (NREL) Simultaneous Saccharification and Fermentation (SSF) Process

The NREL SSF process uses a dilute acid pretreatment (analogous to the steam-explosion process used by Iogen) to render the lignocellulosic matrix susceptible to enzymatic attack. A major improvement is the simultaneous enzymatic hydrolysis and fermentation process. This process continuously removes the sugars from the hydrolysis reactor by fermenting them to produce ethanol. This allows the enzymes to operate efficiently, allowing the use of lower enzyme concentrations, and increasing the concentration of the ethanol which is produced. Also, the NREL system uses genetically engineered *E. coli* bacteria to ferment the five-carbon sugar fraction of the biomass to ethanol, greatly increasing the yield of ethanol. This system was recently analyzed by Chem Systems (Chem Systems 1990 and Hinman *et al.* 1991).

4.2   Methanol Production Technology

Commercial Scale : Koppers-Totzek/Low Pressure Methanol Synthesis

The Koppers-Totzek gasifier, a commercially available gasifier originally developed for use with coal, has been successfully operated on biomass (Chem Systems 1984). The gasifier is an atmospheric pressure, oxygen-steam blown, entrained bed unit which makes a synthesis gas suitable for conversion to methanol. The gasification takes place at very high temperatures (1000°C) and very short residence times. The most serious drawbacks are the need for extensive feedstock preparation to obtain low moisture contents and small particle sizes. Also, the system requires a large oxygen plant.

The methanol synthesis technology a is standard, low-pressure (50-100 atm) process commercially available from either Lurgi or Imperial Chemical Industries (ICI). This process is the basis for nearly all the methanol produced today. Considerable data are available on both processes. The

combination of the Koppers-Totzek gasifier and low pressure methanol synthesis was recently analyzed by Chem Systems for the United States Department of Energy (DOE) (Chem Systems 1989).

Pilot Scale: Institute of Gas Technology (IGT)/Chem Systems Liquid Phase Methanol (LPMeOH) Synthesis

The IGT gasifier is a high-temperature, high-pressure (35 atm), fluidized bed oxygen blown gasifier which uses steam as the fluidizing medium. Because it is a pressurized gasifier, overall power requirements are reduced. The IGT process has the potential to produce a synthesis gas which has the correct H_2/CO ratio for methanol synthesis (eliminating the need for a shift reactor), and which also has a low methane content (eliminating the need for a reformer). The IGT gasifier has been tested at the 1-ton biomass feedstock-per hour scale. However, it still requires the use of an expensive oxygen plant.

The LPMeOH process (has been under development for more than 10 years, and has been tested on a large pilot-scale. In this process, a copper-based catalyst is fluidized or entrained in an inert hydrocarbon liquid. This allows more efficient control over the reactor temperature than is possible in the conventional low-pressure gas-phase process, resulting in higher methanol yields. Also it is not as adversely affected by high CO/H_2 ratios as is the gas-phase process. This combined system was evaluated for the United States DOE by Chem Systems (Chem Systems 1989).

Laboratory and Conceptual Systems: Battelle-Columbus Gasifier w/Low-Pressure Methanol Synthesis

The Battelle-Columbus (BCL) gasifier is a low-pressure, indirectly heated gasifier in which the product char is burned to heat sand, which is in turn mixed with fresh biomass to supply the heat for gasification. This type of gasifier produces synthesis gas with a low H_2/CO ratio, high levels of hydrocarbons, and a low level of carbon dioxide. However, if the hydrocarbons are reformed to produce CO and H_2, the overall yield of useable $CO-H_2$ is higher for this gasifier than for other designs. Also, because it is an indirectly heated gasifier, the expensive oxygen plant is not needed. In this analysis, the BCL gasifier will be paired with the standard low pressure methanol synthesis technology (Wyman, Bain *et al* 1993).

5   Biochemical Conversion of Biomass to Ethanol

This section analyzes the biochemical processes which can be used to convert biomass into ethanol. Because enzymes and cells which carry out the biochemical conversions carry out only specific reactions, an understanding of the nature of the starting material is critical to the process design. Therefore, we first describe the chemical structure of the biomass feedstock. Then, with this information in hand, an overview of the conversion process is presented. Finally, we present detailed analyses of the commercial, pilot-scale, laboratory scale, and conceptual process designs.

5.1   Feedstock Composition and its Implications for the Biochemical Processing of Biomass to Ethanol

Lignocellulosic biomass has a complex structure which has evolved to perform the functions of the living plant. The biomass includes structural elements which provide strength, vascular elements which conduct liquids through the plant, storage cells, and layers which provide protection against degradation. To carry-out these different functions, biomass is built up from several different types of chemical monomers, each of which is best suited to carry out a specific function. Further, in the natural environment, biomass is subjected to continual attack by fungi and other organisms which seek to break it down to simple sugars for use as a food source. Therefore, though the process of evolution, lignocellulosic biomass has developed a structure which is quite resistant to attack.

5.1.1   The Physical and Cellular Structure of Biomass

The basic structural unit of lignocellulosic materials is the cell or fiber. Cells range in length from 0.5 to 3 mm, with longer cells occurring in softwoods and shorter cells in hardwoods (which accounts for the higher value of softwoods in the production of paper products). The cell diameter can range from 20 to 500 μm.

The cross sectional structure of a cell is shown in Figure 5.1. The substance which separates two cells is the middle lamella, which is composed entirely of a protective layer of lignin. The first layer of the actual cell is the primary wall. When the cell is growing, this is essentially pectin, but in mature cells it is primarily a protective layer of lignin, with roughly 10% each cellulose and hemicellulose. Most of the woody substance is contained in the secondary wall. The secondary wall provides strength to the fiber, and is composed primarily of cellulose and hemicellulose (Wenzl 1970, Browning 1963, Panshin and de Zeeuw 1980, Chum et al. 1985).

Cellulose. The largest single component of biomass is cellulose. Cellulose is a linear polymer of D-glucose (a six-carbon sugar) molecules held together by β-glycosidic bonds (Figure 5.2). Chain lengths (degree of polymerization

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or DP) of 10,000 or more are common in native wood. Cellulose fibers are arranged in bundles of parallel chains (microfibrils) in which adjacent chains are bound by hydrogen bonding, forming a crystalline material with great mechanical strength and high chemical stability. Approximately 75% of the cellulose is crystalline, with less chemically resistant

Figure 5.1 Fine structure of hardwood and softwood fibers.

amorphous regions occurring between layers in the secondary wall and at chain ends and surfaces. Because the bond between glucose units is the weak link in the chain, the polymer can be hydrolyzed to glucose, a sugar which is readily fermentable to ethanol.

Cellulose Chain
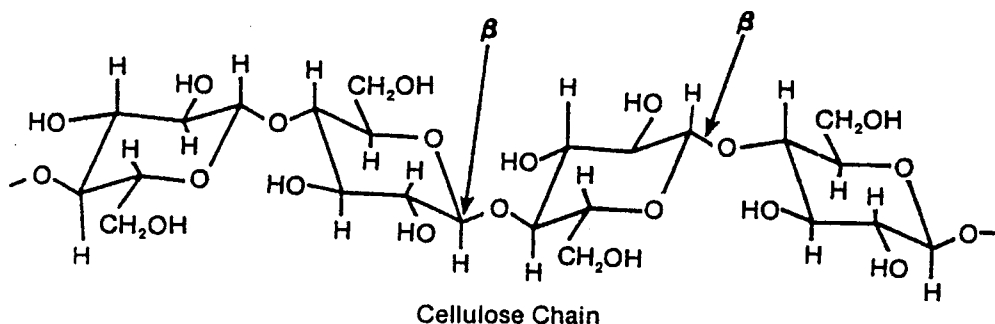
Figure 5.2 Structure of cellulose.

The cellulose is well protected from attack by either chemical or biological agents. The cellulose occurs only in microfibrils, which are tightly bonded together, and highly crystalline. This crystalline cellulose is resistant to chemical attack, and is difficult to hydrolyze, with enzymes or even with high-temperature acid solutions. Further, most of the cellulose is surrounded by a layer of hemicellulose and lignin, and is therefore not readily accessible to either chemical or biological attack.

Hemicellulose. The hemicelluloses are relatively low molecular-weight, non-cellulosic, structural polymers which occur in the plant cells walls along with lignin and cellulose. In spite of the name, hemicelluloses have no chemical

or structural relationship to cellulose. In hardwoods, there are two types of hemicellulose, the xylans and glucomannans. The dominant hemicellulose is xylan, which is a polymer made up of xylose, acetic acid, and methylglucuronic acid. The typical xylan has a DP of 2000, and has an amorphous, highly branched structure. A small fraction of the hemicellulose is an amorphous linear polymer of glucose and mannose, with a typical DP of 100. A typical structure for the dominant xylan hemicellulose is shown in Figure 5.3. The important facts are that approximately 75% of the hemicellulose fraction can be hydrolyzed to give potentially fermentable sugars, while 25% consists of organic acids which are not fermentable to ethanol. Hemicellulose is readily hydrolyzed by dilute acids and high-temperature steam, but not by the enzymes used to hydrolyze the cellulose to glucose. Unfortunately, the major sugar produced by the hydrolysis of hemicellulose (xylose) is not fermentable by the standard ethanol producing yeast (*Saccharomyces cerevisiae*). Therefore, the development of organisms which can ferment xylose have been one of the major objectives of bioconversion research.

Lignin. The non-carbohydrate component of the cell wall is lignin, a polymer largely built on the phenylpropane unit. Lignin in higher plants provides a vascular system for the mechanical reinforcement of the lignocellulosic matrix which transports liquids and solutes over long distances, and provides a defense against biodegradation. The lignin is chemically bound to and mixed with the hemicellulose, and is concentrated in the outer layers of the fiber where it protects the underlying carbohydrates from enzymatic attack.

$$
\begin{array}{ccccc}
\text{3-O-acetyl} & & \text{2-O-acetyl} & & \\
| & & | & & \\
\text{—xyl} & \beta\text{(1-4)xyl} & \beta\text{(1-4)xyl} & \beta\text{(1-4)xyl} & \beta\text{(1-4)xyl—} \\
& | & & | & \\
& \alpha\text{(1-2)} & & \text{3-O-acetyl} & \\
& | & & & \\
& \text{glucuronic acid} & & & \\
& | & & & \\
& \text{4-O-methyl} & & &
\end{array}
$$
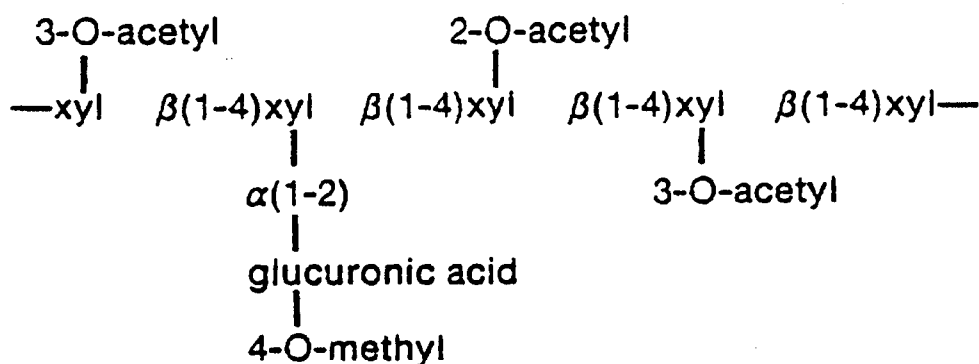
Figure 5.3   Structure of the xylan fraction of hardwood hemicellulose.

Lignins are a random polymer made up of phenylpropane units, where the phenol may be either a guaiacyl or a syringyl unit (Figure 5.4). The units are bonded together in several ways, the most common of which are α or β-ether linkages. A variety of carbon-carbon linkages are also present, but are less common (Figure 5.5).
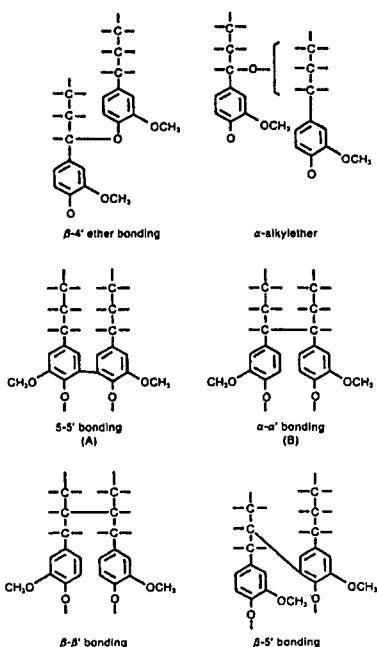
Figure 5.4   Monomer units in lignins.

Because lignin has a hydrocarbon-like structure based on the phenylpropane unit instead of a carbohydrate-based structure like the other major fractions of biomass, it is not fermentable to ethanol. Lignin accounts for 15-35% of the weight of biomass. However, lignin accounts for more of the energy content of the biomass than is obvious from the gross composition because it has a much higher energy per pound than the more highly oxygenated carbohydrates.

5.2   Chemical Composition of Biomass

The chemical and structural composition of the lignin and hemicellulose, as well as the relative proportions of the cellulose, hemicellulose and lignin vary across the different types of biomass. The average composition of some of the major types of biomass are shown in Table 5.1.

The most important point is that the weight fraction of the biomass which is potentially convertible to fermentable sugars ranges from 60-80%, while the energy content of the fermentable sugars is somewhat smaller. Thus, as not all of the energy content of the wood is convertible to alcohol, it is crucial to convert the carbohydrate fraction with a very high efficiency. Also, as the hardwood feedstock is in the middle of the composition range, the results of this study can be extrapolated to other feedstocks with confidence. While there are real and important differences between the processing conditions needed to convert a high lignin substrate such as softwoods and a low lignin easily-digestible herbaceous species such as wheat straw (a plant optimized

β-4' ether bonding   α-alkylether

5-5' bonding (A)   α-α' bonding (B)

β-β' bonding   β-5' bonding
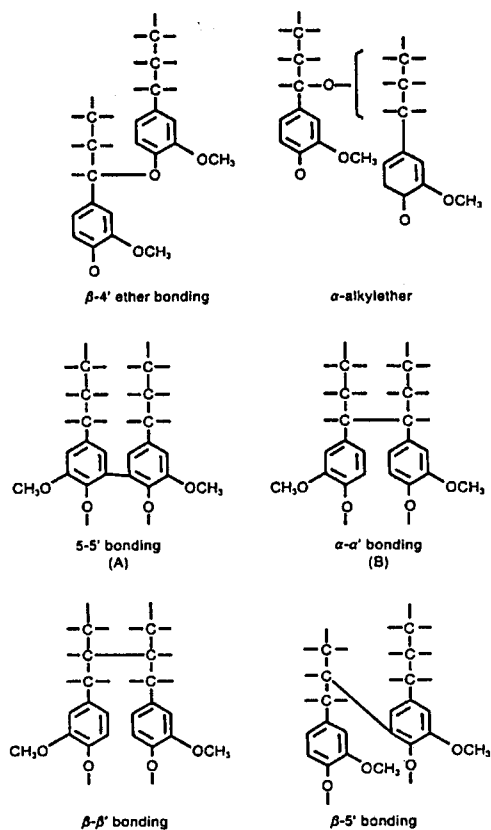
Figure 5.5   Ether and carbon-carbon bonds in lignin.

Table 5.1   Average composition of lignocellulosics (Parisi 1989).

Species	Cellulose (wt %)	Hemicellulose (wt %)	Lignin (wt %)
Conifers (softwoods)	40-50	20-30	25-35
Deciduous trees (hardwoods)	40-50	30-40	15-25
Cane bagasse	40	30	20
Corn cobs	45	35	15
Corn stalks	35	25	35
Wheat straw	30	50	15

to run on wheat straw would operate poorly or not at all on a hardwood or softwood), the differences in equipment design and processing equipment do not greatly affect the overall process economics.

5.3   Overview of the Biochemical Conversion of Biomass to Ethanol

As we saw in the preceding section, although biomass is an inexpensive feedstock, it is chemically complex and difficult to process. The challenge of biochemical processing is to develop low cost methods of breaking the carbohydrate fraction of biomass structure down to simple sugars, and to develop organisms which can convert as many of these sugars as possible to ethanol.
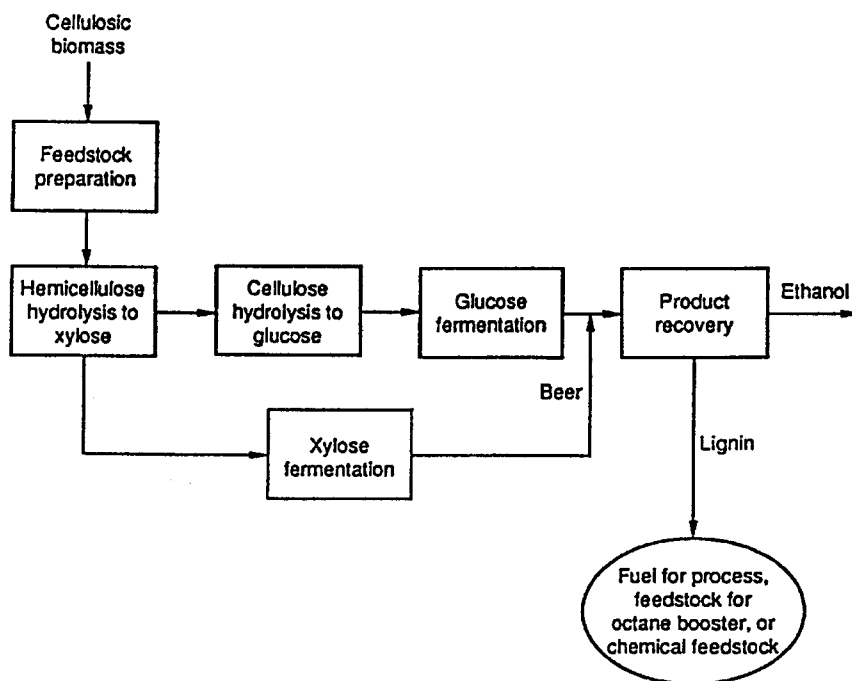
Figure 5.6   Biochemical conversion of lignocellulose to ethanol.

The overall design of processes which convert biomass to ethanol is set by the nature of the feedstock, and includes separate operations to process the cellulose, hemicellulose, and lignin. A general schematic for the overall conversion process is given in Figure 5.6. The lignocellulose is brought to the plant, and pretreated with either high-temperature steam or dilute acid to remove the protective lignin/hemicellulose layers which surround the cellulose. This process also depolymerises (hydrolyses) the hemicellulose, forming an aqueous stream rich in five-carbon sugars, which in the more advanced processes, is fermented to ethanol. The crystalline cellulose and lignin remain behind as a solid residue, relatively untouched by the pretreatment process. The cellulose is then hydrolyzed to glucose by either acid or enzymatic catalyzed hydrolysis. The glucose is then fermented to ethanol and carbon dioxide and combined with the ethanol from the xylose fermentation process. This dilute beer (2-7% ethanol by weight) is then concentrated to fuel grade ethanol by distillation. The lignin, which remains as a solid through both the pretreatment and hydrolysis processes, is dried

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and burned to provide the energy needed to run the process. The remaining unconverted fractions of the feedstock, primarily extractives and organic acids, are sent to the waste treatment process, and may be converted to combustible gases by anaerobic digestion.

5.4 Commercial Scale Technology - Dilute Sulfuric Acid (Percolation) Technology with Glucose Fermentation

The process described in this section (percolation dilute-acid hydrolysis followed by fermentation of the glucose to ethanol) was first developed in Germany in the late 1920s. Improvements on the original Scholler-Tornesch process were made by the United States Department of Agriculture at Madison during World War II (Harris 1945a and 1945b) and by the United States Tennessee Valley Authority (Gilbert et al. 1953). In the 1980s, improvements were made by Inventa A.B. in Switzerland (Mendelsohn and Wettstein 1981), by the New Zealand Forest Research Institute (Uprichard and Burton 1982), and in the United States (Wright 1986a, 1987, Bergeron and Werdene, NREL et al. 1989). In the 1970s and 1980s, approximately thirty percolation-based plants were in operation in the Soviet Union for the production of single-cell protein from hardwoods (Wenzl 1970).

This analysis is based on the engineering analysis of Wright (1984 and 1986a) carried out at the Solar Energy Research Institute (now the National Renewable Energy Laboratory) for the United States Department of Energy. Although the experimental data used to construct the material balance are relatively old (Gilbert 1953), none of the latter studies described above were able to achieve greater yields or higher sugar concentrations. The detailed engineering design was based on a detailed study carried out by Badger Engineers (Badger Engineers 1984), and the cost data were obtained from the Icarus® cost database.

The major features of the process are that it uses a semi-batch, high-temperature, dilute sulfuric acid-hydrolysis process to break down the hemicellulose and cellulose into their component sugars, followed by a standard fermentation process using Saccharomyces cerevisiae to convert the glucose to ethanol. Neither of these processes is very efficient. The hydrolysis process converts roughly 65% of the crystalline cellulose and the six-carbon fraction of the hemicellulose into fermentable sugars. The fermentation is relatively inefficient at converting the six-carbon sugars to ethanol because of the large amount of toxic by-products produced in the acid hydrolysis process, and it is unable to convert the five-carbon sugars (primarily xylose) to ethanol.

The major issues in this process are the hydrolysis of the cellulose and hemicellulose, and the fermentation of resulting sugars to ethanol. Therefore, we address these two aspects in detail in the following two sections, then provide a description of the entire process, and finally analyze and discuss the process economics.

5.4.1 Acid Hydrolysis of Cellulose

One method of breaking down the chemically resistant crystalline cellulose is with high-temperature dilute sulfuric acid. Unfortunately, conditions sufficiently severe to break down the crystalline cellulose are also sufficiently severe to degrade the product sugars. Therefore, sugar degradation is the central problem of dilute acid hydrolysis.

The major reactions of cellulose and hemicellulose degradation are shown below (Harris *et al.* 1985):

Crystalline Cellulose → Glucose → HMF → Tars

Amorphous Cellulose → Crystalline → Glucose → HMF → Tars

Amorphous Xylan → Xylose → Furfural → Tars
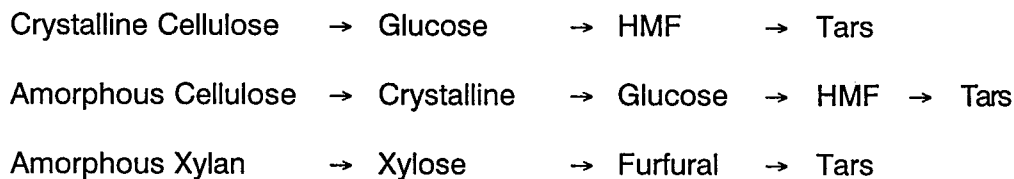
* HMF = hydroxy methyl furfural

The hydrolysis of the amorphous cellulose and xylan can be carried out at low temperatures and acid concentrations (150°C and 1% H_2SO_4) where the conditions are not severe enough to attack either the sugars or the crystalline cellulose. This process is called prehydrolysis and yields of greater than 80% can be achieved on the amorphous components. However, at the higher temperatures needed to hydrolyze the crystalline cellulose sugar, degradation is very rapid.

Unfortunately, at 180°C the rates of cellulose hydrolysis and glucose degradation are approximately equal (reaction time constants of 45 minutes to 1 hour), and yields in a batch reaction are very low. Therefore, to obtain higher yields, the solids are retained in the reactor for several hours to give the cellulose time to fully hydrolyze, while the liquids are kept in the reactor for only 30-45 minutes so that the soluble sugars which are produced are washed from the reactor before they have time to degrade. To accomplish this, the liquid is percolated down though a bed of solid wood chips, and continually removed from the reactor (Figure 5.7). Additionally, for the first hour of operation the water/acid solution entering the reactor is kept at 150°C, a temperature high enough to hydrolyze the hemicellulose, but low enough to minimize the degradation of the xylose and glucose produced during the prehydrolysis process. After the hemicellulose is completely removed, the temperature is then raised to the 180°C needed to hydrolyze the crystalline cellulose.

There are, of course, trade-offs in the design of percolation reactors. The faster the sugars are removed from the reactor, the less time they will have to degrade, and the higher the yields will be. However, higher flow rates will result in dilute sugar solutions, which will in turn result in large equipment and high energy consumption in the distillation section. The optimal trade-off

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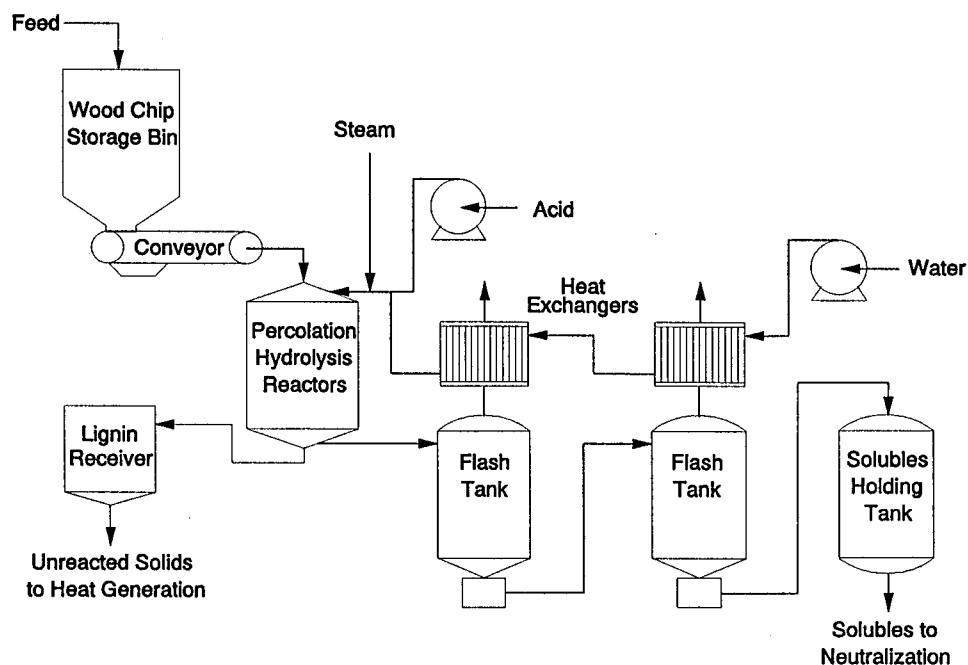
Figure 5.7 Percolation hydrolysis reactor system.

of yield is 55% based on xylose and 63% based on cellulose, and a total sugar concentration in the product of 6%. Thus, approximately 60% of the total carbohydrates are converted into sugars, 10% remain as unreacted solids, and roughly 30% are converted first into sugars and then into degradation products. Unfortunately, many of these degradation products are toxic to microorganisms, and can reduce the rate and yield of the fermentation process.

5.4.2 Glucose Fermentation with *Saccharomyces cerevisiae*

The fermentation organism is the yeast *Saccharomyces cerevisiae*, the most widely used brewing yeast. This organism is very hardy, and tolerates high ethanol concentrations. It ferments the glucose to ethanol by the reaction:

$$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2$$
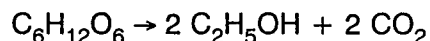
This reaction converts 51% of the weight of the glucose into ethanol. However, the energy efficiency of the fermentation is very high (the heating value of the products divided by heating value of the reactants is 95%). The main drawback of this process is that while *S. cerevisiae* is very efficient at fermenting glucose, it is unable to ferment xylose, the second most plentiful sugar.

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5.4.3   Overall Process Design

The overall process dilute acid hydrolysis process is shown in Figure 5.8, and the key performance parameters are given in Table 5.2. The fresh hardwood feedstock chips are delivered by rail and truck, washed, and transferred to the wood pile.

```
                              Water      Acid
                                        (H₂SO₄)
                                │          │
                                ▼          ▼
  Process      ┌──────────┐         ┌──────────────┐    Unreacted        Heat
────────────► │   Size   │ ──────► │  Hydrolysis   │ ──────────────► Generation
   Feed        │ Reduction│         │               │     Solids
               └──────────┘         └──────────────┘
                                         │
                                    Solubles
                                 (Sugar and Water)
                                         │
                                         ▼
  Ca (OH)₂ ────────────────────► ┌──────────────┐ ──────────► CaSo₄
                                 │ Neutralization│
                                 └──────────────┘
                                    Water
                                    Sugars
                                         │
                                         ▼
  Yeast ──────────────────────► ┌──────────────┐ ──────► Yeast (Single Cell Protein By-Product)
                                 │ Fermentation │ ──────► CO₂ By-Product
                                 └──────────────┘
                                  Ethanol-Water
                                         │
                                         ▼
                                 ┌──────────────┐ ──────► Water
                                 │  Purification │
                                 │ (Distillation)│ ──────► Stillage to Waste Disposal
                                 └──────────────┘
                                         │
                                         ▼
                                     Ethanol
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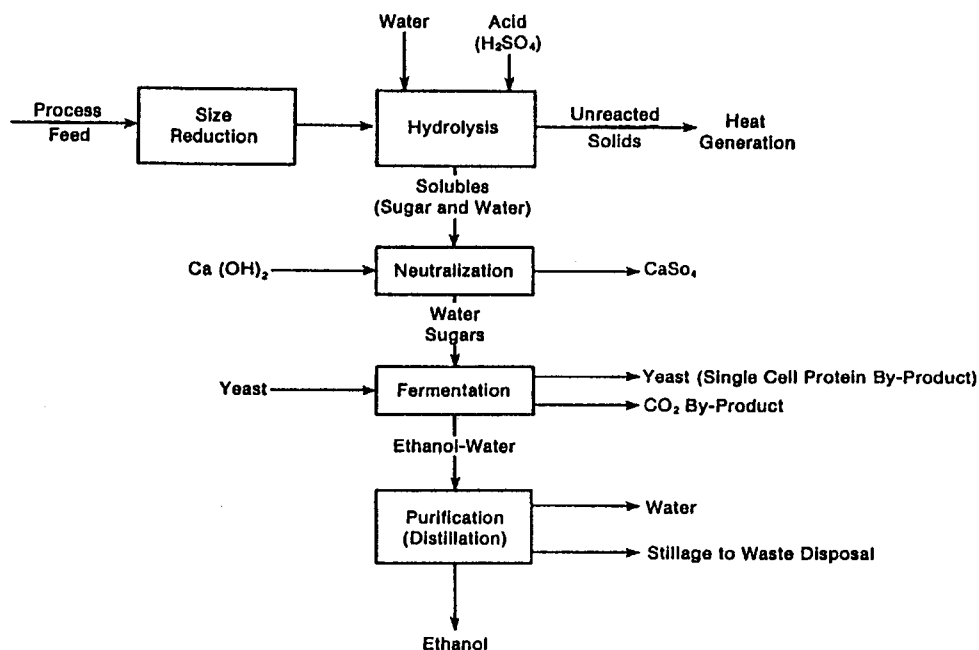
Figure 5.8   Process schematic for percolation high temperature sulfuric acid hydrolysis followed by glucose fermentation.

The chips are then fed directly to percolation hydrolysis reactors, where they are hydrolyzed with 0.5% sulfuric acid at a temperature of 150°C to 185°C. The yield based on six carbon sugars is 63%; the five-carbon sugar yield is 55%.   The hydrolyzate leaving the hydrolysis reactors is flashed to atmospheric pressure in two steps to quench the degradation reactions. The spent wood chips remaining in the reactor after the hydrolysis is completed (consisting primarily of lignin and a small amount of unreacted cellulose) are dumped out of the reactor, dried, and burned to provide the steam and electricity needed to run the plant.

The hydrolyzate from the hydrolysis reactors is neutralized with lime to pH 10, and the pH is then readjusted to near pH 7.   This over-neutralization precipitates many of the sugar degradation products formed during the hydrolysis. Concentrations of residual organics are then further reduced by

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steam stripping (Hajny 1981). Even with these treatments to improve the fermentability of the hydrolyzate, the fermentation efficiency of the hydrolyzates from this process is considerably lower than for the much cleaner enzymatic hydrolysis processes which will be described later (85% vs. 95%).

Table 5.2 Processing parameters for the percolation acid hydrolysis - glucose fermentation ethanol production process.

Hydrolysis	
C_6 hydrolysis efficiency	63%
C_5 hydrolysis efficiency	55%
Outlet sugar concentration (C_6 and C_5)	6%
Fermentation Efficiency	
Glucose to ethanol	85%
Xylose to ethanol	0%
Products	
Ethanol	109E6 l/yr, 28.9E6 gal/yr
Electricity	36 MW
Overall Energy Efficiency	
Ethanol	20%
Ethanol and Electricity	31.3%

The batch fermenters are eight, chemically sterilized 250,000 gallon carbon steel vessels. Yeast (*Saccharomyces Cerevisiae*), is added to the hydrolyzate solution to begin the fermentation. A high yeast density in the tank speeds fermentation, and helps to overcome any inhibitors remaining in the hydrolyzate. Recycle of yeast provides a preacclimatization, and minimizes the cell growth in the fermentation, improving the yield. The fermentation time is 8 hours and the fermentation yield is 85% of the glucose. Xylose and other sugars not fermentable by standard industrial yeasts pass through the fermentation unaffected.

Dilute beer from fermentation is concentrated to 40 weight percent in the beer column. The flow of stillage (xylose, waste organics) from the bottom of the column is pumped to the evaporation section. Distillate is fed to the rectification column, which concentrates the ethanol to its azeotropic composition (91.2 weight percent). The bottoms stream, containing 3.5 weight percent ethanol in water, is recycled to the beer column. Several

components, collectively termed fusel oils, tend to accumulate within the rectification column and are removed in a sidedraw purge. Azeotropic ethanol is dehydrated to 199+ proof by molecular sieve absorption.

In the evaporation section, a three-stage evaporator is used to concentrate stillage to produce a solution of 60% mixed organics in water, which is burned as a liquid fuel to produce steam. About half of the recovered condensate is recycled to the acid hydrolysis unit and about half is sent to anaerobic digestion.

Two boilers are designed to burn solid, liquid, and gaseous fuel byproducts from the process units in order to generate 1100 psia steam for use in the process and for electrical power generation. Gas and liquid fuels are burned directly but lignin and tar sludge from the acid hydrolysis unit is fed to a Flake type drying system which dries and fluidizes the solids into the burners using boiler flue gas. A turbogenerator package unit is rated to take 1100 psia, 825°F steam and generate 45 MW of electricity.

5.4.4   Process Economics

Capital Investment. The capital investment is shown by process area in Table 5.3. The overall capital investment is quite high at $1.77/l of annual capacity ($4.67/gallon) or $58/annual GJ of production. The major reason for this is the inefficiency of the process. A large investment is required to produce a relatively small amount of ethanol. The largest single expense is for the utility section, primarily the boiler and power generation equipment. The point here is that virtually all of the feedstock is eventually burned, and relatively little is converted to ethanol. Other expensive areas include the hydrolysis section (because of the large high-pressure reactors) and the distillation section (because of the dilute ethanol stream which must be processed). A secondary reason for the high capital cost is that because a relatively dilute sugar stream is

Table 5.3   Capital investment by process area of the percolation - glucose fermentation ethanol production process.

Section	Investment (million $)
Feedstock handling	9.9
Hydrolysis	22.1
Fermentation	12.6
Distillation	20.3
Offsite tankage	5.8
Environmental control	18.0
Utilities	46.4
Total investment	**135.0**
Capital Investment/ Unit of Annual Production	**$1.23/ liter-yr $4.67/gallon-yr $58.00/GJ-yr**

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produced, very large volumes of water are processed to produce a relatively small amount of ethanol.

Cost of Production. The cost of production summary (expressed in both $/l, $/gallon and $GJ) is shown in Table 5.4. The dominant costs are those of the feedstock and the capital investment. These are both a result of the low efficiency of the process; only 20% of the energy content of the wood is converted into ethanol. In summary, large amounts of wood are processed and a considerable amount of equipment is needed to produce a small amount of ethanol. Although the overall efficiency of the process is greater when the generation of excess electricity is considered, this power generation is merely making the best of a bad situation. If power generation were the main goal, the wood would be burned directly, not after being ground, soaked in water, hydrolyzed, and dried.

The low process efficiency is a direct result of the low efficiency of the dilute acid hydrolysis process and the fact that only the glucose fraction of the feedstock is fermented to ethanol. As over 50 years of research have not been able to significantly increase the yield of the dilute acid hydrolysis process, it is clear that a fundamentally different hydrolysis process is needed (hence the use of enzymatic hydrolysis in the more advanced processes). Also, it is clear that a means of fermenting the xylose to ethanol is also needed.

5.5   Pilot-Scale Technology - Iogen Enzymatic Hydrolysis Process

Because of the low yields inherent in the dilute acid hydrolysis processes, most of the bioconversion research over the past decade has focused on enzymatic hydrolysis processes. The primary advantage of enzymatic hydrolysis is that the cellulase enzymes carry out only one reaction, the hydrolysis of cellulose to glucose, and do not catalyze the destruction of the glucose. Thus, enzymatic hydrolysis has the potential to convert a very large fraction of the feedstock into ethanol.

The process described in this section is a first generation enzymatic hydrolysis process, and one of the few which has been carried out at the pilot scale. The Iogen (Canada) process has been carried out at the 1 ton per day scale, while most other enzymatic hydrolysis processes are still at the laboratory scale of investigation.

The Iogen process uses a high-temperature steam pretreatment to prepare the feedstock for the enzymatic hydrolysis. The enzymes used to break down the cellulose to ethanol are produced by fungi which are grown on a lactose (cheese whey) carbon source. The hydrolysis is carried out, and then the hydrolyzate is sent to a separate set of vessels where the glucose is fermented to ethanol. As in the previous case, the fermentation yeast is S. cerevisiae, and the xylose is not fermented to ethanol.

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Table 5.4   Ethanol cost of production summary by percolation hydrolysis with glucose fermentation.

	¢/liter	¢/gallon	$/GJ
Raw Materials			
Wood (kg)	25.6	97.0	12.10
Sulfuric acid	2.2	8.2	1.03
Lime	1.15	4.37	0.54
Chemicals	0.85	3.2	0.40
Utilities			
Water	0.3	1.21	0.14
Electricity	-7.8	-29.7	-3.70
Labor	1.5	5.5	0.71
Maintenance	3.7	14.0	2.04
Overhead	4.0	15.2	2.10
Insurance, Property taxes	1.8	7.0	1.05
Total annual operating costs	**33.3**	**126.0**	**16.04**
Total capital charges (@30%)	**37.1**	**140.3**	**17.53**
Cost of Production	**70.4**	**266.3**	**33.30**

1 GJ = 0.948 MMBtu

The data on this process were taken from a study of the Iogen process carried out by Douglas (1989) for Energy, Mines and Resources Canada. The study was based on data from the Iogen pilot plant. Much of the cost data were derived from the same Icarus® results used in the analysis of the dilute acid hydrolysis process described above. Other groups have carried out analyses of enzymatic hydrolysis processes which are very similar to the Iogen process, notably Wright, Power and Douglas (1986), A.D. Little (1985), and Stone & Webster Engineers (1987). While differing in the details, these studies arrive at consistent results.

5.5.1   Enzymatic Hydrolysis of Cellulose

Before describing the detailed system used by Iogen, it is useful to understand the technology of enzymatic hydrolysis. All enzymatic processes consist of four major steps that may be combined in a variety of ways: pretreatment, enzyme production, hydrolysis, and fermentation (Figure 5.9). Pretreatment opens up the structure of the lignocellulose so that the enzymes can reach and attack the cellulose, reducing the time needed for hydrolysis from weeks, months, or years, to a few hours. In enzyme production, fungi are grown to produce the enzymes necessary to hydrolyze the feedstock. In

hydrolysis, enzymes break the cellulose down to glucose, which is then fermented to ethanol.
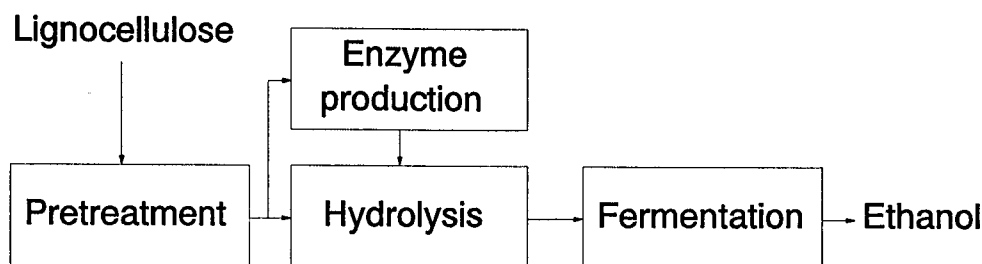
Figure 5.9   Fungal enzyme hydrolysis.

Pretreatment. It has long been recognized that some form of pretreatment is necessary to achieve reasonable rates and yields in the enzymatic hydrolysis of biomass. This has generally been attributed to the crystallinity of cellulose, the lignin hemicellulose-sheath that surrounds the cellulose, and the lack of available surface area for the enzymes to attack. Originally, mechanical pretreatments such as intensive ball or roll milling were investigated as means of increasing the surface area, but they required exorbitant amounts of energy. In the past decade, attention has been focused on chemical methods. The efficiency of chemical methods can be understood by considering the interaction of the enzymes and the substrate. The hydrolysis of cellulose into sugars and oligomers is a solid-phase reaction in which the enzymes must bind to the surface to catalyze the reaction. Cellulase enzymes are large proteins with molecular weights ranging from 30,000 to 60,000, and are thought to be ellipsoidal with major and minor dimensions of 30 and 200 angstroms. While the internal surface area of wood is very large, only 20% of the pore volume is accessible to the large cellulase molecules. By breaking down the hemicellulose-lignin matrix, the hemicellulose or the lignin can be removed and the accessible volume greatly increased. This greatly enhances enzymatic digestibility.

The hemicellulose-lignin sheath can be disrupted by either acid or basic catalysts. Basic catalysts simultaneously remove both lignin and hemicellulose, but suffer large consumption of base through neutralization by the ash and acid groups in the hemicellulose. Most work in recent years has focused on acid catalysts, which can be mineral acids or organic acids generated *in-situ* by the autohydrolysis of the hemicellulose.

Autohydrolysis Steam Explosion. Understanding that enzymatic digestibility is related to removal of material and increase in pore size, we can understand the trends that have emerged from this research. Most important is the trade-

off between reaction time and temperature. Equal solubilization of hemicel-lulose can be achieved at high temperatures and low residence times, or lower temperatures and longer residence times. Good hydrolysis results have been achieved in both regimes. However, if large chips are used, heat transfer problems may result in overcooking of the outside of the chip and incomplete autohydrolysis in the interior. Also, very high-temperature processes may lead to significant pyrolysis, which produces inhibitory compounds. High-temperature reactors require close control over residence time, since sugar degradation becomes significant after 1 minute at 270°C. Lower temperatures (190°-200°C) and longer residence times (10 minutes) are favored by some investigators. However, because the ratio of the rates of hemicellulose hydrolysis to sugar degradation is greater at high temperatures, low-temperature processes have lower xylose yields and produce somewhat more degradation products than a well-controlled high-temperature process using small particles. In general, xylose yields in autohydrolysis are low (30-50%). An autohydrolysis system is used as the pretreatment in the Iogen process discussed in this section.

An important advantage of the autohydrolysis process is that it breaks the lignin into relatively small fragments that can be easily solubilized in either base or organic solvents. For example, roughly 80% of the lignin in steam treated aspen wood is solubilized in 0.4 wt % sodium hydroxide.

Dilute-Acid Prehydrolysis. Lower temperature operation with reduced sugar degradation can be achieved by adding small amounts of mineral acid to the pretreatment process. The acid increases the reaction rates and increases the ratio of the hydrolysis rate to the degradation rate. Acid pretreatments have been studied in the United States (Torget *et al.* 1987) and Canada (Brownell 1986). A similar tradeoff between reaction temperature and time exists for acid-catalyzed reactions as for autohydrolysis. Acid catalysts have also been used in so-called steam explosion systems with similar results. Xylose yields generally range from 70-95%. However, the sulfuric acid processes produce a lignin that is more condensed (52% of the lignin extractable in dilute sodium hydroxide) than that produced by autohydrolysis processes. The Simultaneous Saccharification and Fermentation (SSF) process described in section 5.6 below (the conceptual case) uses a dilute acid pretreatment.

Pretreatment Summary. By understanding the function and trade-offs involved in acid-catalyzed pretreatments, we can evaluate their effect on the overall lignocellulose-to-ethanol process. As will be shown later, the capital and operating costs of a well-designed pretreatment section are not a large fraction of the total ethanol production cost. Therefore, the importance of pretreatment is primarily its effect on the performance of the downstream processes, particularly hydrolysis and xylose fermentation.

Enzyme Production. Enzyme production can be a very costly section of the lignocellulose-to-ethanol system. High costs arise from the low rate of

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enzyme production and the need for large amounts of enzyme. The amount of enzyme used can be minimized by changes to the hydrolysis section: operating at the minimum enzyme loading, recycling enzyme, and maximizing yield, and by combining the enzyme hydrolysis and fermentation processes to relieve end product inhibition. The second approach is to improve the production process itself.

Most of the cellulase-producing fungi under investigation today are related to *Trichoderma reesei (viride)*, first isolated at the United States Army Natick Laboratories. Since then, many mutants have been produced. Most prominent among these is the Rut C-30, the first mutant with greatly increased β-glucosidase production. Other advantages of the strain are that it is hyperproducing (produces amounts of cellulase greater than that needed for culture growth) and is catabolite-repression resistant.

Enzyme production with *T. reesei* is difficult because cellulase production is usually discontinued in the presence of easily metabolizable substrates. Thus, most production work has been carried out on insoluble carbon sources such as steam-exploded biomass. In such systems, the rate of growth and cellulase production is limited because the fungi must secrete cellulase and carry out a slow enzymatic hydrolysis of the solid to obtain the necessary carbon. The best results in such systems have been achieved in fed-batch systems where the substrate is slowly added to the fermented so as not to provide an excess of substrate. Average productivities have been approximately 100 IU/L-h steam-exploded agricultural residues and 50 IU/L-h on steam-exploded aspen wood. However, productivities of approximately 400 IU/L-h have been reported by logen in a fed-batch system using lactose as a carbon source and steam-exploded aspen as an inducer. Increases in productivity dramatically reduce the size and cost of the fermenters used to produce the enzyme.

Another aspect of fungal cellulases is their extremely low specific activity. Most fungal cellulases have specific activities near 0.6 IU/mg (although some strains are approximately twice this), while commercial amylases (enzymes which hydrolyze starch) have activities of 100 IU/mg. Increases in the specific activity of the enzyme would have an effect similar to that of increasing the productivity.

Enzymatic Hydrolysis. Before discussing the details of the hydrolysis process itself, it is useful to survey the mechanism of cellulose hydrolysis. The overall hydrolysis is based on the synergistic action of three distinct cellulase enzymes: endo-β-glucanases, exo-β-glucanases, and β-glucosidases. Endo-β-glucanases (Figure 5.10) attack the interior of the cellulose polymer in a random fashion, exposing new chain ends. Because this enzyme catalyzes a solid-phase reaction, it absorbs strongly but reversibly to the crystalline cellulose. The strength of the absorption is greater at lower temperatures. This enzyme is necessary for the hydrolysis of crystalline substrates. Exo-β-glucanases remove cellobiose units (two glucose units)
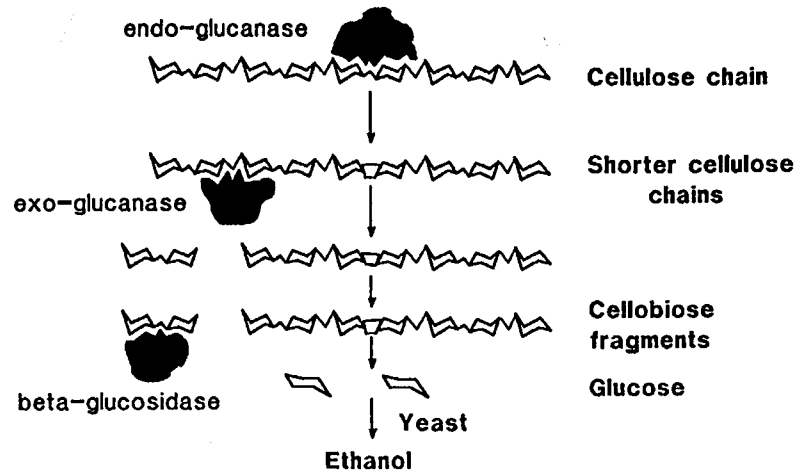
Figure 5.10 Mechanism of enzymatic hydrolysis and simultaneous saccharification and fermentation (SSF).

from the nonreducing ends of cellulose chains. This is also a solid-phase reaction, and the exoglucanases absorb strongly on both crystalline and amorphous substrates. As these enzymes continue to split off cellobiose units, the concentration of cellobiose in solution may increase, which may severely inhibit or stop the action of the exo-glucanases.

The cellobiose is hydrolyzed to glucose by the action of β-glucosidase. This is a liquid-phase reaction, and β-glucosidase absorbs either weakly or not at all on cellulosic substrates. The action of the β-glucosidase can be slowed or halted by the accumulation of glucose in solution. This accumulation may also bring the entire hydrolysis to a halt as inhibition of the β-glucosidase results in a build-up of cellobiose, which in turn inhibits the action of the exoglucanases. The hydrolysis of cellulosic materials depends on the presence of the proper amounts of all three enzymes. If any one of the enzymes is present in less than the required amount, the other enzymes will be inhibited or lack the necessary substrates to act on.

The hydrolysis rate increases with increasing temperature. However, because the catalytic activity of an enzyme is related to its shape, deformation of the enzyme at high-temperature can inactivate or destroy the enzyme. To strike a balance between the increased activity and the increased deactivation, it is preferable to run fungal enzymatic hydrolysis processes at approximately 45-50°C.

5.5.2 Iogen Process Design

The overall process flow sheet for the Iogen process is shown in Figure 5.11 and the major processing parameters are listed in Table 5.5. The raw chips are delivered to the plant by rail or truck. The chips are transported by conveyor from the storage area to the steam explosion feed bins, which provide surge capacity between the continuous conveyor system and the batch steam explosion (autohydrolysis) guns. The pretreatment section consists of four steam explosion guns, each of which fires once every 22 seconds. A single cycle consists of loading the gun from the hopper, injecting 235°C steam, cooking the chips at temperature for five seconds, and explosively decompressing the chips into a flash drum. As described in the previous section, this process hydrolyses much of the hemicellulose,
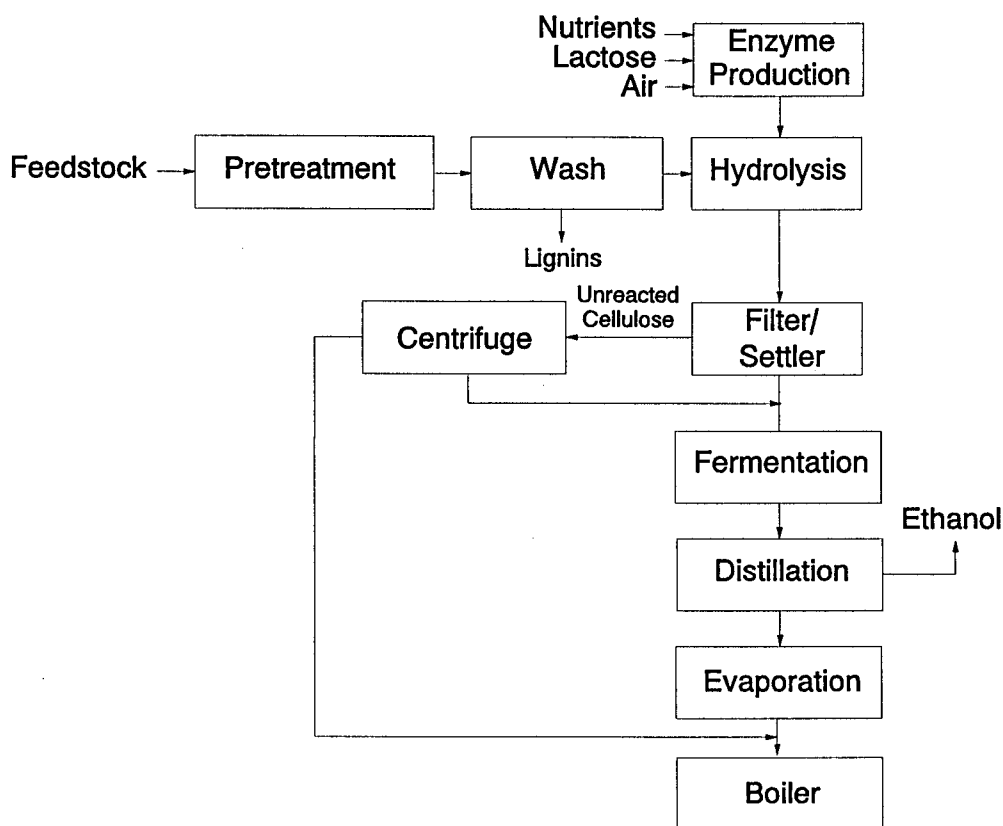
Figure 5.11 Schematic of the Iogen enzymatic hydrolysis process.

increases the surface area, and renders the wood susceptible to enzymatic attack. The pulp is then processed in a counter-current water/alkali wash which removes the hemicellulose sugars (which were solubilized in the steam explosion process), and removes many of the degradation products which

were formed in the autohydrolysis. (The amount of toxic degradation products produced in the steam explosion process is much less than in the percolation acid hydrolysis process.) The cleaned pulp, which now consists primarily of cellulose, is then sent to the hydrolysis section.

Table 5.5 Processing parameters for the Iogen enzymatic hydrolysis process.

Pretreatment	
Steam explosion autohydrolysis	235°C for 5 seconds
Enzymatic Hydrolysis	
Enzyme loading	25 IU/gm cellulose
Solids loading	16 weight %
Residence time	72 hours
C_6 yield	85%
Glucose concentration in outlet	8.8%
Enzyme Production	
Productivity	400 IU/l-hr
Fermentation	
Glucose to ethanol	95%
Xylose to ethanol	0%
Products	
Ethanol	168 E6 liter/year 44.4 E6 gallons/year
Electricity	13.6 MW
Overall Energy Efficiency	
Ethanol	30%
Ethanol and Electricity	34%

The enzyme production section uses a *T. reesei* mutant optimized to grow on lactose. Lactose is a considerably more expensive substrate for growth that pretreated cellulose, but allows much higher fungal growth rates and enzyme productivities. The enzyme production tanks are quite expensive, as they are operated at pressure to improve oxygen transfer to the rapidly growing fungi.

The enzymatic hydrolysis section uses a fed batch process. In order to achieve high sugar concentrations and thereby minimize the amount of water which must be handled, it is necessary to process a slurry with a very high concentration of cellulose. Unfortunately, mixtures which contain more than 10% cellulose are essentially solid pastes, and are virtually impossible to stir

or pump. Therefore, an initial slurry of approximately 8% solids is prepared, and the enzymes are added to initiate the hydrolysis process. After several hours have passed, some of the cellulose has been converted to soluble sugars, and the initial near solid mass becomes quite liquid. Thereafter, additional batches of cellulose are added to the reactor over the course of the 72-hour hydrolysis. The net effect is equivalent to processing a 16% solid slurry. After the hydrolysis is completed, the hydrolyzate is sent to the fermentation tanks and the unreacted solids are dried and burned to produce steam and electricity.

The batch fermentation uses the yeast *S. cerevisiae* to convert the glucose to ethanol. The fermentation efficiency is higher than in the dilute acid case because the hydrolyzate is much cleaner. Also, the product ethanol concentration is higher because the input glucose concentration from hydrolysis is higher. However, the xylose fraction of the feedstock is still not converted to ethanol. The remainder of the plant (environmental systems, utilities, and boilers) are identical to those described in the previous sections.

5.5.3   Process Economics

Capital Investment. The capital investment by process area is shown in Table 5.6. As in the dilute acid hydrolysis case the capital investment is still quite high at $1.1/liter of annual capacity ($4.54/annual gallon). In this case, however, the reasons are somewhat different. Because of the improved hydrolysis yield, the logen process produces 50% more ethanol from a given amount of feedstock than does the dilute acid process. However, the capital equipment is quite expensive. This results from the need for a pretreatment section to make the biomass digestible by the enzymes (not needed in the acid hydrolysis process), the very high cost of enzyme production (the hydrolysis process uses large amounts of enzymes and operates at above atmospheric pressure), and the large and expensive tanks in the hydrolysis section. Thus, unlike the dilute

Table 5.6   Capital investment by process area for the logen enzymatic hydrolysis process.

Section	(million $)
Feedstock handling	14.0
Pretreatment	20.0
Enzyme production	44.0
Hydrolysis	23.0
Fermentation	3.7
Distillation	6.1
Offsite Tankage	7.0
Environmental	12.0
Utilities	53.3
Total Investment	**182.0**
Capital Investment/ Unit of annual production	**$1.08/liter-yr $4.54/gallon-yr $51.2/GJ-yr**

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acid case, the problem is not as much low yield, as it is the need for expensive equipment.

<u>Cost of Production.</u> The cost of production for the Iogen enzymatic hydrolysis process Table 5.7 is $0.63/liter or $2.40/gallon. The dominant costs are the capital investment and the feedstock. The absolute contribution of the feedstock to the cost of production is considerably reduced from that in the previous case (17¢/liter vs. 26¢/liter) because of the higher yield of the enzymatic hydrolysis process. While the credit for excess power production is lower, this is because the ethanol yield is higher, and not as much of the feedstock is burned. As discussed above, the contribution of the capital investment to the cost of production is large, both because the conversion efficiency is low (while the efficiency is better than for acid hydrolysis, 30% is still a very low number in absolute terms), and because the equipment used to carry out the enzymatic hydrolysis is expensive.

Table 5.7   Cost of production summary for the Iogen enzymatic hydrolysis process.

	¢/l	¢/gallon	$/GJ
Raw Materials			
Wood (kg)	16.7	63.1	7.89
Cheese whey (kg)	3.8	14.3	1.8
Chemicals	2.5	9.5	1.20
Utilities			
Water	0.12	0.46	0.10
Electricity	-1.9	-7.2	-1.0
Labor	1.0	3.6	0.50
Maintenance	3.6	13.6	1.7
Overhead	3.4	12.8	1.6
Insurance, Property taxes	1.8	6.8	1.05
Total annual operating costs	**30.9**	**117.0**	**14.8**
Total capital charges (@30%)	**32.4**	**122.6**	**15.4**
Cost of Production	**63.3**	**239.6**	**30.2**

1 GJ = 0.948 MMBtu

There is considerable room for improvement in the enzymatic hydrolysis process. One of the most promising is the combination of the enzymatic hydrolysis and fermentation processes in a single vessel. In this system (known as simultaneous saccharification and fermentation), the yeast

converts the glucose to ethanol as soon as it is produced. This reduces end product inhibition of the enzymes by the sugars, allows a reduction in the amount of enzyme needed, and can lead to increased yields and sugar concentrations, reduced capital costs, and reduced risks of contamination. Equally important is the development of an organism capable of fermenting the xylose to ethanol, and thereby increasing the yield. Other potential improvements include the development of a more active enzyme complex which can be rapidly grown on pretreated wood and wood sugars, and a host of small process improvements. The next section will describe a system which incorporates such improvements.

5.6 Laboratory Scale Technology - National Renewable Energy Laboratory (NREL) Simultaneous Saccharification and Fermentation (SSF) Process

The process described in this section combines the enzymatic hydrolysis and fermentation into a single operation in order to reduce the inhibition of the enzymatic process by the product sugars, and incorporates a xylose fermentation process as well as a variety of incremental improvements. This process is currently under development at the United States National Renewable Energy Laboratory (NREL). All of the major process steps have been run at the bench-scale, but as of this writing, integrated testing of the process has not been reported. A process which is essentially identical in overall design, but which has an improved performance (better than has currently been achieved, but which can reasonably be expected to be achieved with further research and development) is described in the next section (Section 5.7), and is referred to as the conceptual technology case.

This analysis is based on a report prepared by Chem Systems for NREL (Chem Systems 1990). The report was based on representative bench-scale results (not the best ever achieved, but reproducible values which form a conservative basis for design). The cost estimates are primarily from direct vendor quotations obtained by Chem Systems. Other analyses of SSF processes have been carried out by Wright (1988) and, Hinman and Wright (1989) show results which are consistent with the Chem Systems analysis.

5.6.1 Simultaneous Saccharification and Fermentation

The rationale for the SSF process is to relieve the end-product inhibition produced by the accumulation of glucose and cellobiose in the hydrolyzate. If the hydrolysis and fermentation processes are combined, the yeasts will metabolize the glucose as soon as it is produced. This relieves the end product inhibition of the β-glucosidase enzyme by glucose, which will in turn reduce the buildup of cellobiose, the most powerful of the inhibitors. Further improvements may be possible by using a mixed culture of an ethanol tolerant yeast such as *S. cerevisiae* with a cellobiose fermenting yeast such as *Bretannomyces clausenii*. This strategy directly relieves the end-product inhibition of the endo-glucanase by cellobiose, further reducing the need for high enzyme loadings to overcome end-product inhibition.

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5.6.2 Xylose Fermentation

Because xylose accounts for 30-60% of the total potentially fermentable sugars in hardwoods and herbaceous biomass, it is important to be able to ferment it to ethanol. At the beginning of the 1980's there were no known methods for efficiently converting xylose to ethanol, there are now several potential methods, including alternate yeasts, bacteria, fungi, and combination enzyme-yeast systems (Hinman and Wright 1989).

Bacteria were the first organisms found that can carry out this xylose fermentation. In bacterial fermentation, xylose is converted to xylulose inside the cell by the enzyme xylose isomerase. Then, xylose is used by the main glycolytic pathway and fermented to ethanol. This system is in balance inside the cell, with no net consumption or production of NADH or NADPH, and the theoretical yield is 0.51 g ethanol/g of xylose, the same as in glucose fermentation.

In practice, yields with naturally occurring xylose fermenters are lower than this. Bacteria have many fermentation pathways and can make ethanol, glycerol, lactic and acetic acids. Because these by-products are produced in appreciable quantities with the amounts determined by fermentation conditions, yields of ethanol in bacterial systems have been somewhat lower than those in traditional yeast fermentations. A further problem of most bacterial fermentations is that their ethanol tolerance is low, usually near 1.5%. Recently, many of these problems have been overcome with the genetic modification of the bacteria *E. coli* to ferment xylose. This modified bacteria has high fermentation rates, the ability to produce high ethanol concentrations, and has low by-product production.

Yeast and fungi ferment xylose by a different pathway. Although many yeasts use xylose aerobically, few can use it anaerobically. Fermentation is enhanced when small concentrations of oxygen are present (microaerophilic conditions). This is necessary because there is a discrepancy between the production and consumption of NADH in the conversion of xylose to ethanol, and that the NADH required must come from another pathway that requires small amounts of oxygen to occur. Because of the use of oxygen and the need to produce NADH to carry out the conversion, the theoretical yield of ethanol from xylose is 10% lower than in bacterial fermentations or glucose fermentation by yeast (46 g ethanol/g xylose).

In practice, yeasts have shown higher yields and ethanol tolerance than most bacteria. A great number of investigators have studied yeast xylose fermentations, notably with the organisms *Pachysolen tannophilus*, *Candida shehatae*, and *Pichia stipitis*.

Fewer data are available about fungi. Most of the research has been carried out on the fungi *Fusarium oxysporum*. This organism has high yields when

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ethanol concentrations are under 1-1.5%, but ethanol tolerance limits its use to such very low concentrations.

A final method for carrying out the conversion uses both yeasts and enzymes. Through genetic engineering it is possible to use bacteria such as *E. coli* to produce large amounts of the enzyme xylose isomerase. This enzyme can either be immobilized or used in solution to convert the xylose into xylulose, which can then be used by a large number of yeast to produce ethanol. The advantage of this system would be that its theoretical yield should be 0.51 g ethanol/g xylose, the same as is found in conventional fermentations. The major problem in the system stems from the fact that the pH optima of the yeast is 4-5, while the optima of the enzyme is 6-7.

5.6.3   Process Description

The flow schematic for the "base case" SSF-xylose fermentation process is shown in Figure 5.12, and the major process parameters are shown in Table 5.8. The wood chips from storage are milled to 1-3 mm in a disc refiner, and sent to the dilute acid prehydrolysis system. The wood is impregnated with dilute sulfuric acid at 100°C for 10 minutes, and then sent to the prehydrolysis reactor where it is held at 160°C for 10 minutes. In this process, 80% of the xylan is converted to xylose, 13% is degraded to furfural, and 7% remains unreacted. The crystalline cellulose remains largely untouched in this process; 3% is converted to glucose. The digesters are based on Black-Clawson designs used in the pulp and paper industry. After the solids are discharged from the reactor, they are neutralized with lime and diluted to 12% solids.

The entire stream is then sent to xylose fermentation where the xylose is fermented to ethanol in a continuous process using a genetically modified version of *E. coli* developed at the University of Florida. The yield of ethanol from xylose is 90% with a 2-day residence time.

The stream from xylose fermentation is then sent to the SSF process section. A slipstream of the hydrolyzate is used as the carbon source for the fungal enzyme production, which has a yield of 202 IU/gram cellulose, and requires a 5.5-day residence time.

The enzyme stream from the enzyme production system is combined with the water-cellulose-ethanol stream from the xylose fermentation and sent to the SSF process. As described above, by combining the hydrolysis and fermentation systems, end-product inhibition of the enzyme by the product sugars is greatly reduced, and the amount of expensive enzymes needed in the hydrolysis section is greatly reduced. As a result, this system uses an enzyme loading of only 7 IU/gram, compared with 25 IU/gm cellulose for the Iogen process in which the hydrolysis and fermentation are carried out separately. The continuous SSF system has a cellulose to ethanol yield of 72% in 7 days (a conservative number). Thirteen percent of the original cellulose remains unreacted, 5% is converted to oils, glycerol and
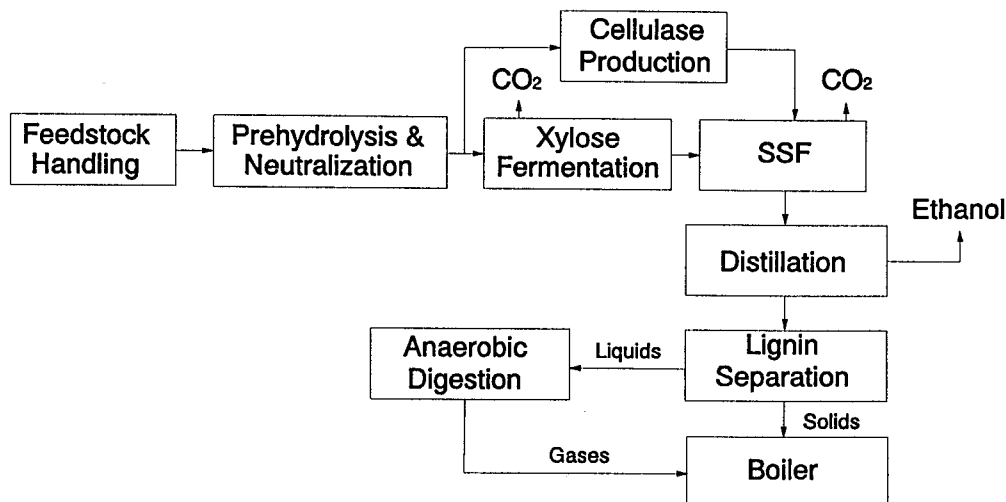
Figure 5.12 Schematic of the NREL SSF-xylose fermentation process.

acetaldehyde, and 10% is incorporated into the yeast cell mass.

The stream from the SSF process is sent to the distillation section where the ethanol is taken overhead and the water and solids (lignin and inorganics) are removed from the bottom. The solids are separated from the liquids, dried and burned, and the liquids are sent to anaerobic digestion.

5.6.4   Process Economics

Capital Investment. The capital investment by process area is shown in Table 5.9. The capital investment is considerably lower than that of the separate hydrolysis and fermentation process described in the previous section. There are several reasons for this. Most important is the reduction in enzyme loading brought about by the combination of the enzymatic hydrolysis and fermentation processes. Another improvement is the elimination of a number of washing and solid-liquid separation steps. Other than the utilities section, which still must handle over 50% of the energy content of the feedstock, the two most important contributions to the capital cost are the prehydrolysis section (for which further cost reductions are unlikely) and the SSF section (which has a very large residence time).

Table 5.8 Processing parameters for the NREL SSF-xylose fermentation process.

Pretreatment	
Dilute acid prehydrolysis	160°C for 10 minutes
Xylose Fermentation	
Xylose conversion to ethanol	90%
Residence time	2 days
Ethanol concentration at outlet	1.5%
Simultaneous Saccharification and Fermentation	
Enzyme loading	7 IU/gm cellulose
Solids loading	12 weight %
Residence time	7 days
C_6 yield to ethanol	72%
Ethanol concentration in outlet	4.5%
Enzyme Production	
Residence time	5.5 days
Products	
Ethanol	219 E6 liter/year 57.9 E6 gallons/year
Electricity	13.3 MW
Overall Energy Efficiency	
Ethanol	39%
Ethanol and Electricity	43%

Cost of Production. The cost of production estimate for the base case SSF-xylose fermentation process is shown in Table 5.10, and is $0.37/liter or $17.3 GJ ($1.34 gallon). The capital investment is now the dominant cost, accounting for almost 50% of the entire cost of production, while the feedstock cost accounts for another 35%. However, in absolute terms these two costs are considerably lower than in the previous case. The capital investment per unit of product has been reduced by roughly 50%, with 60% of the reduction caused by a decrease in the capital investment (primarily by reducing the enzyme production costs and eliminating separation steps) and 40% of the reduction caused by increasing the production rate over which the capital investment must be allocated.

There remains considerable room for improvement even in this process. Among the potential improvements are increased SSF yields, and reduced

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reaction times. The effect of these improvements are described in the final case.

5.7 Advanced System - National Renewable Energy Laboratory (NREL) Simultaneous Saccharification and Fermentation (SSF) Process (Advanced Case)

This section describes an advanced version of the NREL SSF-xylose fermentation process described above. This section is based on the analysis of Hinman *et al.* (1991) at NREL, who carried out sensitivity studies to determine the effect of research improvements on the previous process. The parameters for this process design represent performance which is better than that achieved in the laboratory to-date, but which might reasonably be achieved with further research and development.

Table 5.9 Capital investment by process area for the NREL SSF-xylose fermentation process.

Section	(million $)
Feedstock handling	7.2
Pretreatment	23.7
Xylose fermentation	6.2
Enzyme production	2.8
Hydrolysis	20.9
Distillation	4.0
Offsite Tankage	4.1
Environmental	4.0
Utilities	53.2
Misc.	2.5
Total Investment	**128.4**
Capital Investment/ Unit of annual production	**$0.59/liter-yr $2.22/gallon-yr $27/GJ-yr**

5.7.1 Process Design

The basic flowsheet for the "advanced case" SSF-xylose fermentation is identical to that shown in Figure 5.12, and the important process parameters are shown in Table 5.11.

The yield related performance changes include raising the SSF cellulose to ethanol conversion from 72% to 90% and increasing the xylose to ethanol conversion from 90% to 95%. Improvements which decrease the capital cost include decreasing the SSF residence time from 7 days to 2 days, decreasing the xylose fermentation time from 2 to 1 day, and decreasing the time required for cellulase production from 5.5 to 2 days. Miscellaneous improvements include decreasing the energy consumption in the milling section by 35% and increasing the fraction of time the plant is on-stream from the assumed 90% to the 95% typical of large corn-based ethanol-production plants.

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Table 5.10 Cost of production estimate for NREL SSF xylose fermentation process (base case).

	¢/l	¢/gallon	$/GJ
Raw Materials			
Wood (kg)	12.8	48.3	6.05
Sulfuric acid and lime	0.5	2.0	0.23
Chemicals	1.9	7	1.10
Utilities			
Water	0.0	0.2	0.0
Electricity	-1.5	-5.6	-0.70
Labor	0.7	2.8	0.33
Maintenance	1.8	6.7	0.40
Overhead	1.9	7.3	1.10
Insurance, Property taxes	0.9	3.3	0.43
Total annual operating costs	**19.0**	**72.1**	**9.10**
Total capital charges (@30%)	**17.6**	**66.5**	**8.31**
Cost of Production	**36.6**	**138.6**	**17.3**

1 GJ = 0.948 MMBtu

5.7.2   Process Economics

Capital Investment. The capital investment for the "advanced case" process is shown in Table 5.12. Due to the improvements in the assumed rate of the SSF process, xylose fermentation, and enzyme production process, the absolute capital cost is reduced by 18%. Perhaps the interesting fact is that almost 45% of the total capital investment is now accounted for by the utility section, primarily the boiler-turbogenerator. Thus, we see that for these process parameters we are approaching the point where there is little room left for reductions in the capital investment.

Cost of Production. The calculated cost of production for the "advanced case" ethanol process is $0.26/liter or $0.997/gallon (Table 5.13). The cost of production has been reduced by 28%, primarily because of the increased production, and to a much lesser extent, because of the rates and subsequent decreased capital investment. The biomass to ethanol energy efficiency of this process is 50%, which is 70% of the maximum theoretically possible for a biological conversion process using a hardwood feedstock. Thus, while the potential for yield improvement is not yet exhausted, room for further improvements is limited, and will be more difficult to achieve.

Table 5.11   Processing parameters for the "advanced case" NREL SSF-xylose fermentation process.

Pretreatment	
Dilute acid prehydrolysis	160°C for 10 minutes
Xylose Fermentation	
Xylose conversion to ethanol	95%
Residence time	1 day
Ethanol concentration at outlet	1.5%
Simultaneous Saccharification and Fermentation	
Enzyme loading	7 IU/gm cellulose
Solids loading	12 weight %
Residence time	2 days
C_6 yield to ethanol	90%
Ethanol concentration in outlet	4.5%
Enzyme Production	
Residence time	2 days
Miscellaneous improvements	
Decrease power for feedstock milling by 35%	
Increase on-stream time from 90% to 95%	
Products	
Ethanol	280 E6 liter/year 74.1 E6 gallons/year
Electricity	10.6 MW
Overall Energy Efficiency	
Ethanol	50%
Ethanol and Electricity	54%

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5.8 Additional Potential Improvements in the Production of Ethanol from Biomass

The potential exists for improvements beyond those described in this section. For example, in the basic process of fungal enzyme hydrolysis described in the pilot and advanced cases, the potential exists to reduce the power and capital investment required for the pre-treatment process, improving the methods used to grow the fungi and yeast which carry out the bioconversion processes, and to use advanced bio-reactor designs.

If one moves beyond processes based on hydrolysis with enzymes produced by fungi, there is the potential to use cultures of a single organism of organisms which can simultaneously produce the enzymes and ferment the resulting sugars to ethanol. Such processes are generally referred to as direct microbial conversion (Lynd 1990). Such systems have the advantages of greatly simplifying the process flow sheet, and using the energy derived by the bacteria from the fermentation process to produce the enzymes. Also, bacterial cellulases have been reported to have a much higher specific activity than fungal cellulases. However, to-date the bacterial systems have suffered from poor selectivity (they produce a variety of products other than ethanol), and an inability to produce or tolerate high ethanol concentrations.

The fundamental problem with all biochemical conversion systems proposed to-date is their inability to ferment lignin to ethanol, which results in a low overall conversion efficiency. While this problem cannot be overcome by improved bioconversion processes, it may be possible to develop fast growing herbaceous energy crops with higher fractions of fermentable sugars, and lower lignin and extractive contents.

Table 5.12 Capital investment by process area for the "advanced case" NREL SSF-xylose fermentation process.

Section	Investment (million $)
Feedstock handling	7.2
Pretreatment	23.7
Xylose fermentation	3.7
Enzyme production	1.7
Hydrolysis	8.2
Distillation	4.0
Offsite Tankage	4.6
Environmental	3.9
Utilities	46.4
Misc.	2.1
Total	**105.5**
Capital Investment/ Unit of annual production	**$0.38/liter-yr $1.42/gallon-yr $17.8/GJ-yr**

Table 5.13 Cost of production summary for the "advanced case" NREL SSF-xylose fermentation process.

	¢/l	¢/gallon	$/GJ
Raw Materials			
Wood (kg)	10.0	37.7	5.02
Sulfuric acid and lime	0.5	1.8	0.23
Chemicals	1.6	6.0	1.05
Utilities			
Water	0.0	0.2	0.0
Electricity	-1.0	-3.6	-0.50
Labor	0.6	2.2	0.30
Maintenance	1.1	4.3	0.52
Overhead	1.3	5.1	1.01
Insurance, Property taxes	0.6	2.1	0.30
Total annual operating costs	**15.1**	**57.0**	**7.13**
Total capital charges (@30%)	**11.3**	**42.7**	**5.34**
Cost of Production	**26.3**	**99.7**	**12.43**

1 GJ = 0.948 MMBtu

5.9 Sensitivity Analyses

The uncertainty in the absolute value of the ethanol price is a result of the individual uncertainties in the technical assumptions, the capital cost estimates, the feedstock cost, and the economic assumptions. In this section we illustrate the effect of these uncertainties on the estimated cost of production.

Figure 5.13 illustrates the sensitivity of the cost of production to changes in the required capital recovery factor (CRF) and the feedstock cost. As described in Section 3.5.2, different companies may use internal rates of return and economic assumptions which result in capital recovery factors ranging from 20% to 40% per year. Because of the dominant effect of capital investment on the cost of production, such a change in CRF can result in a ±25% change in the cost of production. Additionally, if we assume that the CRF is constant, the uncertainty band shown in Figure 5.13 for the change in CRF would also correspond to the change in the cost of production caused by a ±30% uncertainty in the capital cost.

The effect of feedstock cost on the cost of production is much smaller. A 20% variation in feedstock cost around the base case ($46/dry tonne) results

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in only a 10% change is the estimated cost of production. Thus, the results
of the analysis are relatively insensitive to the feedstock cost.
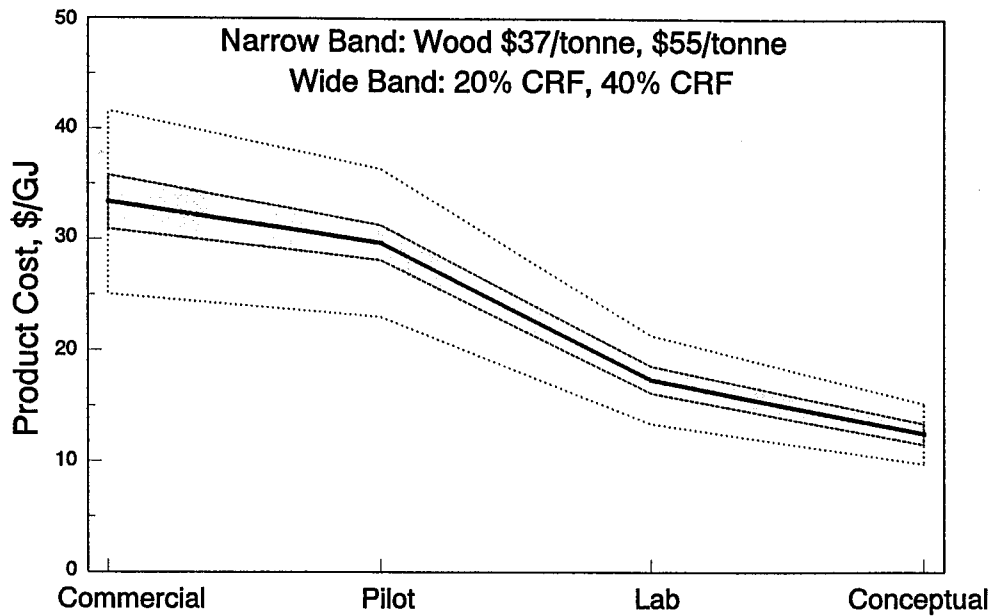
Figure 5.13 Sensitivity analysis for the biochemical conversion of biomass
to ethanol.

The effect of the size of the conversion facility on process economics is
shown in Figure 5.14. In addition to our base case of 1818 dry tonne/day,
we estimated the economics feed rate of process plants sized for 800 and
5,000 tonne/day of feed. As expected, for a constant feedstock cost, the
larger plant has a lower capital investment per annual unit of production, and
thus has a lower cost of production. However, a factor of 2.5 increase or
decrease in size reduces or increases the cost of ethanol production by less
than 10%.
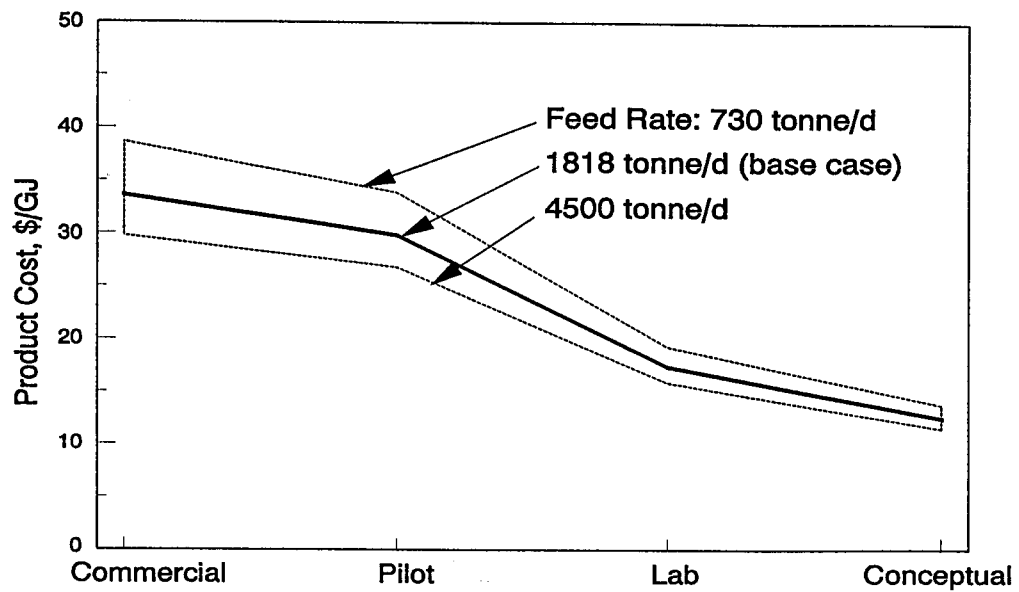
Figure 5.14 Effect of scale on cost of the biochemical conversion of biomass to ethanol.

5.10   Summary of the Biochemical Conversion of Biomass to Ethanol

The economics of the four biomass to ethanol processes are summarized in Figure 5.15. The cost of production ranges from $0.65 liter or $2.46/gallon ($32.5/GJ) for the commercially demonstrated acid hydrolysis process, to $0.25/liter or $0.95/gallon ($12/GJ) in the conceptual case. In all cases, the cost of production is dominated by the contribution of the capital investment. Even in the advanced case, the feedstock accounts for only a little more than one-third of the total cost. By far the most important factor in determining the cost of producing ethanol from biomass is the process efficiency; the fraction of the energy content of the biomass which is converted into ethanol. This is illustrated in Figure 5.16, which shows that the cost of ethanol is inversely proportional to the conversion efficiency.
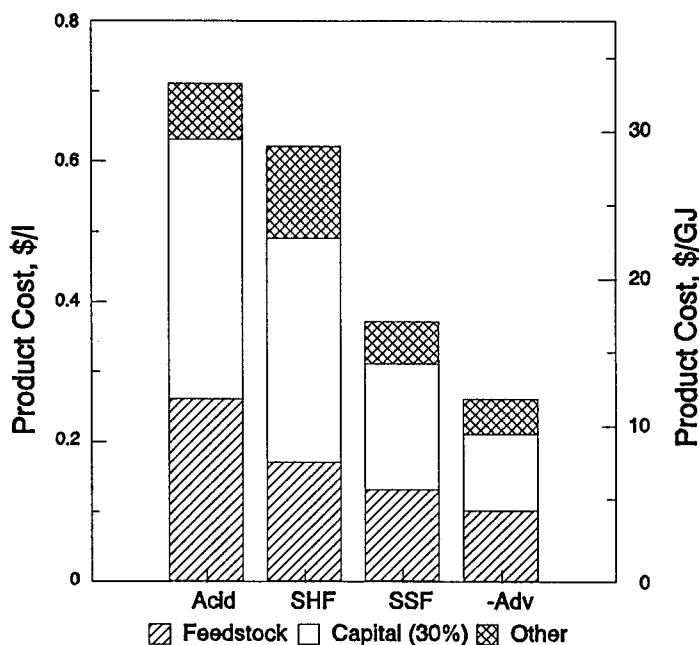
Figure 5.15   Economic summary of biomass to ethanol processes.
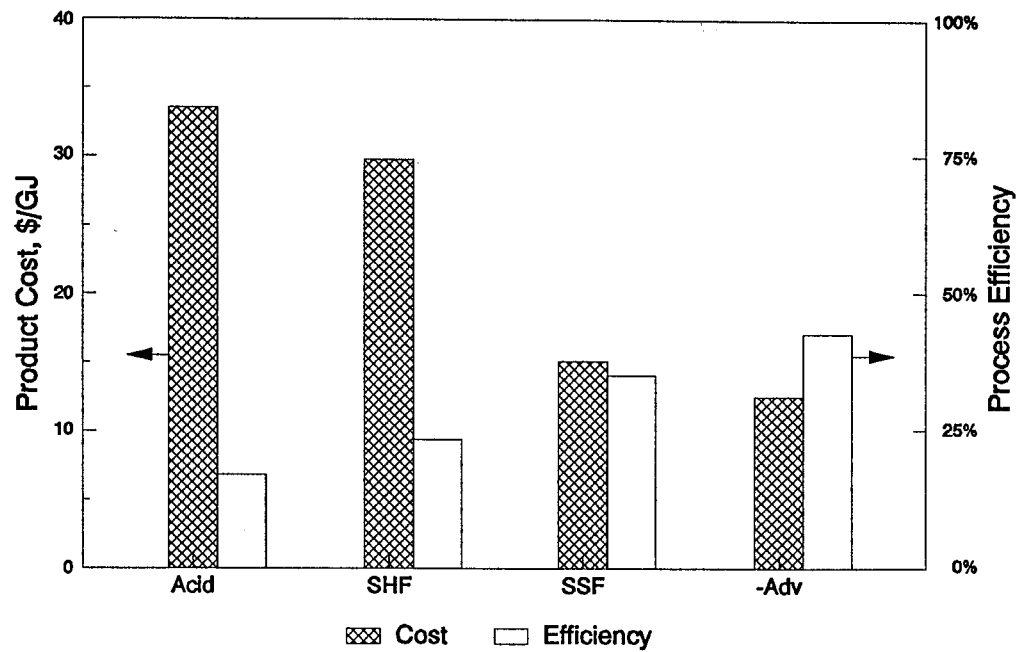
Figure 5.16 Ethanol production/cost and efficiency.

6 Thermochemical Conversion of Biomass to Methanol

This section analyzes the thermochemical conversion of biomass to methanol at four different levels of technology development. As in the previous section, we first discuss the composition of biomass and how it affects the conversion process, then provide a brief overview of the conversion technology. This is followed by detailed analyses of the commercial, pilot scale, laboratory and conceptual level designs.

6.1 Feedstock Composition and its Implications for the Thermochemical Conversion of Biomass to Methanol

The chemical and physical characteristics of biomass which are of most consequence in thermochemical conversion processes are the composition (both elemental and proximate), and the moisture content, particle size and density (Chem Systems 1989, SERI 1979).

6.1.1 Chemical Composition

The chemical composition of woods and coals are often characterized according to their proximate and elemental composition and their heat of combustion. Typical data on several different types of biomass as well as coal and municipal solid waste are presented in Table 6.1.

Proximate Analysis. The proximate analysis classifies the fuel in terms of its moisture content (M), volatile matter (VM), ash (A), and fixed carbon (fixed C) which is given by difference. In the test procedure, the volatile material is driven off by heating the solid sample to 950°C at a slow heating rate. This essentially carries out a slow pyrolysis of the material. In general, the higher the ratio of VM to fixed carbon, the more reactive the feedstock. More reactive feedstocks do not need as high a residence time in the gasifier. As can be seen from Table 6.1, biomass is considerably more reactive than coal. Also, the proximate analysis of many different types of biomass are virtually identical, suggesting that unlike biochemical conversions, processing conditions are not a strong function of the species of feedstock processed.

Elemental Analysis. The ultimate or elemental analysis determines the energy content of the fuel, and affects the downstream processes in which the synthesis gas will be converted to methanol. The energy content of the biomass increases with increasing hydrogen and carbon contents, and decreases with increasing oxygen content. The composition also affects the processing required to convert the syngas to methanol. The ratio of C:H:O in biomass on a molar basis is 1:1.5:0.75, while that of methanol is 1:4:1. Thus, we see that biomass is hydrogen-deficient compared with methanol. (As we will see in Section 6.2, this is the rationale for the use of the water-gas shift reaction, which exchanges carbon monoxide for additional hydrogen.)

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Table 6.1 Composition of selected biomass feedstocks, coal and municipal solid waste (MSW) (Chem Systems 1990a, Domalski et al. 1987)

	Hardwood Maple	White Pine Sawdust	Balsam Spruce	Millrum Bagasse	Bituminous Coal Low Volatiles	Bituminous Coal High Volatiles	Average Urban Refuse
Proximate analysis, wt %							
Moisture	*	7.0	3.67	49	3.6	3.56	18.4
Volatile matter	76.1	78.76	77.75	-	17.41	37.18	75.3
Fixed C	19.6	14.1	15.52	-	74.84	56.55	10.8
Ash	4.3	0.14	3.06	2	4.14	2.71	13.9
Ultimate analysis, wt %							
C	50.4	52.32	53.3	48.2	83.68	79.61	41.2
H	5.9	6.05	6.65	6.7	4.57	5.54	5.5
O	39.1	40.05	35.05	45.1	5.73	9.83	30.7
N	0.5	0.56	1.49	-	1.12	1.61	0.5
S	0.0	0.39	0.20	-	0.76	0.70	0.2
Ash	4.1	0.15	3.18	2.0	4.14	2.71	13.9
Higher heating Value (kJ/kg)	19,914	20,995	22,560	20,164	33,686	33,055	19,835
Particle density, g/cc	0.68	0.43	0.45	-	1.35	1.35	-

* Dry basis analysis, typically moisture content is 50 wt percent on a wet basis.

We also see that biomass has a much higher hydrogen and oxygen content than coal, and that the elemental composition of a wide variety of biomass feedstocks is quite similar.

The ash and sulfur contents of biomass are quite low. Thus, the treatment required to ready the syngas from biomass gasification for methanol synthesis is considerably less expensive than that required with coal gasification. Likewise, the lower ash content results in reduced problems and costs for ash disposal.

6.1.2 Physical Characteristics

Water Content. The moisture content of biomass is considerably higher than that of coal. As delivered to the plant, biomass may have a moisture content as high as 50% (compared with 3-6% in coal). This water must be driven-off with waste heat prior to the biomass entering the gasifer.

Size and Density. The size and density of the biomass particles affect the performance of the gasifier. Most existing gasifiers require a finely divided feedstock, both to allow rapid heat transfer to the biomass particle and because the flow of biomass through the gasifier is strongly dependent on particle size. Therefore, the size of the biomass particles must be reduced prior to gasification. Because biomass has a fibrous structure and is not crushable like coal, size reduction processes for biomass are generally more capital- and energy-intensive than those for coal. Also, the low density of

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biomass particles increases the potential in some gasifier types for undersized particles to be entrained with the product gases.

6.2   Overview of the Thermochemical Conversion of Biomass to Methanol

The major steps in the production of methanol from biomass are: gasification, gas clean-up and shift/reforming, CO_2 removal, and methanol synthesis (Figure 6.1). In the gasification step, the solid biomass is heated in the presence of steam and/or oxygen and converted to raw syngas, a mixture of CO, H_2, CO_2, H_2O, and hydrocarbons. The gas is then cleaned to remove tars and particulates. Because the C:H ratio of biomass is too low for optimal methanol synthesis, steam is added to the raw syngas, converting CO and H_2O to CO_2 and H_2 over a shift catalyst, with the net effect of trading CO for H_2. It may also be advantageous to steam reform the methane and other hydrocarbons in the raw syngas to obtain additional CO and H_2. The CO_2 and sulfur-containing acid gases are then removed. The clean syngas is sent to methanol synthesis, where the carbon monoxide and hydrogen are catalytically combined to produce methanol.

Biomass

Gasification

Shift/ Reforming

CO₂ Removal → **CO₂**

Methanol Synthesis
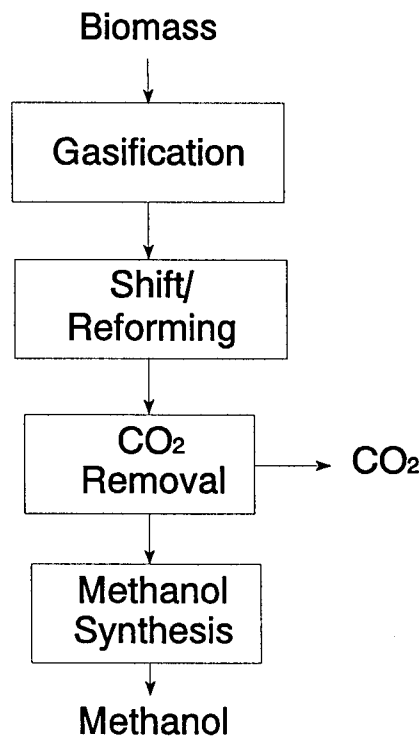
Methanol

Figure 6.1   Overall biomass to methanol process.

6.2.1   Gasification

Prior to gasification the feedstock is dried and sized. In general, waste heat is used to dry the biomass to 5% to 15% moisture. In general, the heat required to dry the biomass from 50% moisture to 10% moisture amounts to roughly 10% of the lower heating value of the wood. The size of the particles entering the gasifier varies greatly depending on the gasifier design. Entrained-bed gasifiers, such as the Koppers-Totzek, require 0.5 mm (minus 30 mesh) particles. Fluidized-bed gasifiers can tolerate a larger range of sizes, although fines may be carried out of the bed before they have enough time to react.

Gasification is carried out in an atmosphere of steam and/or oxygen at temperatures near 1400 K, at pressures of 1-25 atmospheres with a residence time of 0.5-20 seconds (or longer in the case of fixed-bed gasifiers). Many reactions occur simultaneously in the gasifier, including:

$$C + O_2 \xrightarrow{-94.3} CO_2 \qquad \text{Oxidation}$$

$$CO + H_2O \xrightarrow{-8.3} CO_2 + H_2 \qquad \text{Water-Gas Shift}$$

$$C + 2 H_2 \xrightarrow{-21.5} CH_4 \qquad \text{Methane formation}$$

$$C + H_2O \xrightarrow{+32.5} CO + H_2 \qquad \text{Gasification}$$

$$C + CO_2 \xrightarrow{+40.8} 2 CO \qquad \text{Gasification}$$
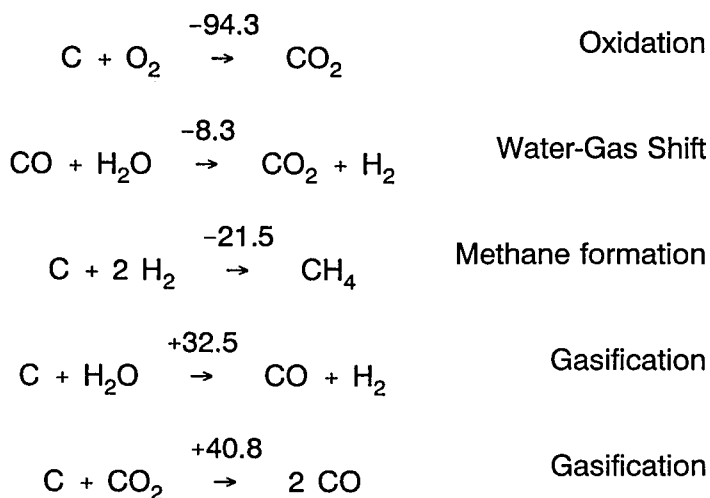
where the heats of reaction are given in kcal/g-mole. In simplified terms, the exothermic oxidation of the biomass (which can occur either inside or outside the gasification reactor) provides the heat needed to drive the endothermic gasification reactions of carbon with hydrogen, water and carbon dioxide (Probstein 1982).

Biomass may be gasified by partial oxidation (where oxygen is injected directly into the gasifier), or by thermal pyrolysis (where heat is supplied from an external source to drive the reactions of steam with biomass). With less reactive feedstocks (such as coal), partial oxidation with oxygen must be used to achieve reasonable reaction rates. Three different gasifiers have been analyzed in this study: the Koppers-Totzek (K-T) and IGT "Renugas" gasifiers (partial-oxidation gasifiers), and the Battelle-Columbus indirectly heated gasifer.

Partial-oxidation gasifiers inject oxygen into the gasifier to provide the heat needed to drive the reactions. (Air blown gasifiers are not suitable for methanol production because the methanol synthesis process uses a very large recycle ratio and cannot tolerate large amounts of inert materials.) These gasifiers operate at higher temperatures than indirectly heated gasifiers and therefore produce a syngas with a low methane content which does not need reforming before it enters the methanol production reactor. However, the oxygen plant is one of the most expensive items in the entire process. Oxygen produced by a large and efficient cryogenic air separation plant typically costs $44-$66/tonne (Drnevich et al. 1981, Chem Systems 1990c). As a typical partial-oxidation gasifier uses 0.25-0.3 kg of oxygen per kg of dry feedstock, the oxygen cost would be $11-$20 per ton of wood processed. Thus, the cost for oxygen in partial-oxidation gasifiers is very large, approximately 24%-44% of the cost of the biomass feedstock itself. Oxygen-blown gasifiers have been built in the entrained bed, fluidized bed, and fixed-bed modes, and have been operated at scales of 5-100 tonne wood per day. Oxygen-blown gasifiers which have been used with biomass include the IGT gasifier in the United States, the Creusot-Loire facility in France, and the Biosyn gasifier in Canada (Evans et al. 1988, Chrysostome and Lemasle 1983).

Indirect gasifiers use external combustors to provide the heat needed to drive the gasification reactions. Depending on the design, the heat is added either through tube bundles embedded in the reactor or by circulating a stream of inert solids. The main advantage of the indirect gasifiers is that they separate the combustor and gasifier, and thereby eliminate the need to use pure oxygen combustion to prevent the introduction of nitrogen into the system. By eliminating oxygen usage, both capital and operating costs are greatly reduced. However, at the lower gasification temperatures typical of indirectly heated gasifiers, a large amount of methane is produced. Thus, a reforming step is required to convert the methane and hydrocarbons leaving the gasifier into the CO and H_2 needed in the methanol synthesis process (Feldman 1988, Rensfelt and Ekstrom 1989, MTCI 1990).

6.2.2 Syngas Conditioning

In the syngas conditioning steps the raw gas is cleaned and the H_2/CO ratio is adjusted. First, particulates are removed by cyclones, wet scrubbing or high-temperature filters. For gasifiers which produce significant amounts of hydrocarbons, the hydrocarbons must be steam reformed to produce additional CO and H_2 by reactions such as:

$$CH_4 + H_2O \rightarrow CO + 3\ H_2$$
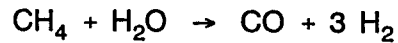
The gases are then passed through the water-gas shift reactor where the reaction

$$CO + H_2O \rightarrow CO_2 + H_2$$
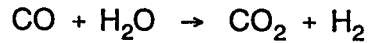
trades CO for additional H_2, and increases the H_2/CO ratio to two. After leaving the water-gas shift reactor the gases are cooled and the CO_2 and sulfur containing acid gases are removed (Philp 1986).

6.2.3   Methanol Synthesis

The clean gases with a H_2/CO ratio of two are then sent to methanol synthesis where carbon monoxide and hydrogen are combined to produce methanol according to the highly exothermic reaction

$$CO + 2\,H_2 \rightarrow CH_3OH$$
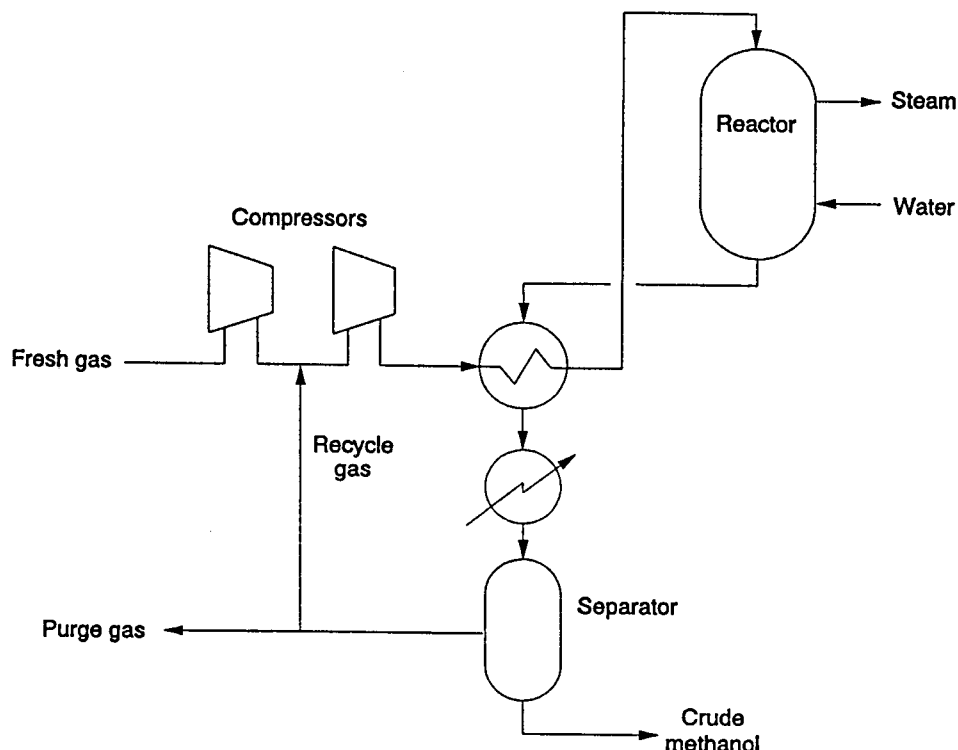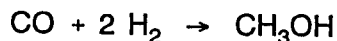
Figure 6.2   Simplified methanol synthesis schematic.

The reaction is carried out at 230°C-300°C and pressures of 50-100 atmospheres. The reaction is equilibrium limited, and 25%-30% of the reactants are converted per pass through the reactor. After each pass, the product gases are cooled, the methanol is removed by condensation, and the remaining gases are recycled to the reactor (Figure 6.2). Both major process vendors [Lurgi and Imperial Chemical Industries (ICI)] use fixed catalyst beds to carry out the reaction. ICI uses injections of cold gas at various points in the reactor to control the temperature, while Lurgi uses tubes of catalyst surrounded by a pressurized water boiler. Because of the high recycle rate, a purge stream is needed to prevent the build-up of methane, CO_2 and other inert gases. Thus, unless the amount of inerts entering the methanol synthesis system is minimized, large amounts of CO and H_2 can be lost with the purge stream.

The methanol product contains water as well as small amounts of other organics. For fuel methanol, a simple, one-column distillation system is sufficient to reduce the water content, and the higher alcohols are blended into the fuel. If higher quality methanol is needed for chemical purposes, a two- or three-column system is used to separate and recover the water and higher alcohols (Fiedler *et al.* 1990, Herman 1986).

6.2.4 Overall Process Efficiency

The energy required to drive the highly endothermic gasification reactions comes from the oxidation (combustion) of a fraction of the biomass (either in the gasifier in the case of partial oxidation gasifier or in a separate combustor in the case of the indirectly heated designs). In either case, the energy used in the combustion process can not be used to produce methanol, and therefore results in a reduction in the potential process efficiency. On the other hand, the methanol synthesis process is highly exothermic, liberating heat which is used to drive a variety of process steps. If the energy released in the endothermic methanol synthesis reaction could be used to drive the gasification reactions, and the gas conditioning operations required no energy input, the maximum theoretical energy efficiency of the biomass to methanol process would 95%. This is virtually identical to the efficiency of the sugar to ethanol fermentation which has very similar stoichiometry. However, because the gasification reaction occurs at high temperatures (roughly 1000°C) while the methanol synthesis reaction occurs at low temperatures (230°C to 300°C), the energy produced in methanol synthesis can not be used to drive the gasification process. Therefore, the maximum theoretical efficiency of the biomass to methanol process is on the order of 52% to 58%, depending on the reactions which are employed in the gasification process.

6.3 Commercial Scale : Koppers-Totzek/Low Pressure Methanol Synthesis

The process described in this section uses the commercially available Koppers-Totzek gasifier. This gasifer was originally developed for use with coal, and approximately 50 gasifiers of this type have been installed in 19 different sites around the world. Most installations have used bituminous coal or lignite as a feedstock, but heavy naphtha, fuel oil, refinery gasses and peat have also been used. The gasifier has been tested at full scale on wood, but the K-T gasifier has not been used commercially with wood. The gasifer is coupled to a standard low-pressure methanol synthesis process of the type licensed by either ICI or Lurgi. Taken together, these two processes account for well over 90% of the world's installed methanol capacity. Thus, while all the components of this system have been used in commercial practice, the entire system has never been run in an integrated manner.

This analysis is based on a report recently carried out by Chem Systems for the United States Department of Energy (Chem Systems 1989). The cost data are primarily from vendor quotes.

6.3.1   Overall Process Design

The process flow schematic for the K-T Low Pressure Methanol Synthesis process is shown in Figure 6.3. The hardwood feedstock is dried to 5% moisture in four parallel rotary drum driers using waste heat from the reformer flue gasses, and then ground to minus 30 mesh (600 μm) in two trains of three grinders. Although this is a very energy-intensive operation, it is necessary because of the low residence time entrained bed design of the K-T gasifier.

```
                          ┌──────────┐
                          │  Oxygen  │
                          │  Plant   │
                          └──────────┘
                                                              50°C
┌──────────┐   ┌──────────┐   ┌──────────────┐   ┌─────────┐   ┌──────────┐
│   Wood   │───│   Wood   │───│ Gasification │───│ Cooling │───│  Solids  │
│  Drying  │   │ Grinding │   │              │   │         │   │ Removal  │
└──────────┘   └──────────┘   └──────────────┘   └─────────┘   └──────────┘
                                  1000°C                             │
                                  1 atm                        ┌──────────────┐
                                                               │ Intermediate │
                                                               │ Compression  │
                                                               └──────────────┘
                                                                      │
                                                               ┌──────────────┐
                                                               │   CO Shift   │
                                                               │  Conversion  │
                                                               └──────────────┘
                                                                      │
                                                               ┌──────────────┐
                                                               │   Cooling    │
                       75 atm                                  └──────────────┘
                       250°C                                          │
           ┌──────────────┐  ┌──────────┐  ┌─────────────┐       ┌──────────┐  CO₂
Methanol ◄─│   Methanol   │──│ Methanol │──│    Final    │  50°C │ Acid Gas │
           │ Distillation │  │ Synthesis│  │ Compression │───────│ Removal  │─► H₂S
           └──────────────┘  └──────────┘  └─────────────┘       └──────────┘
```
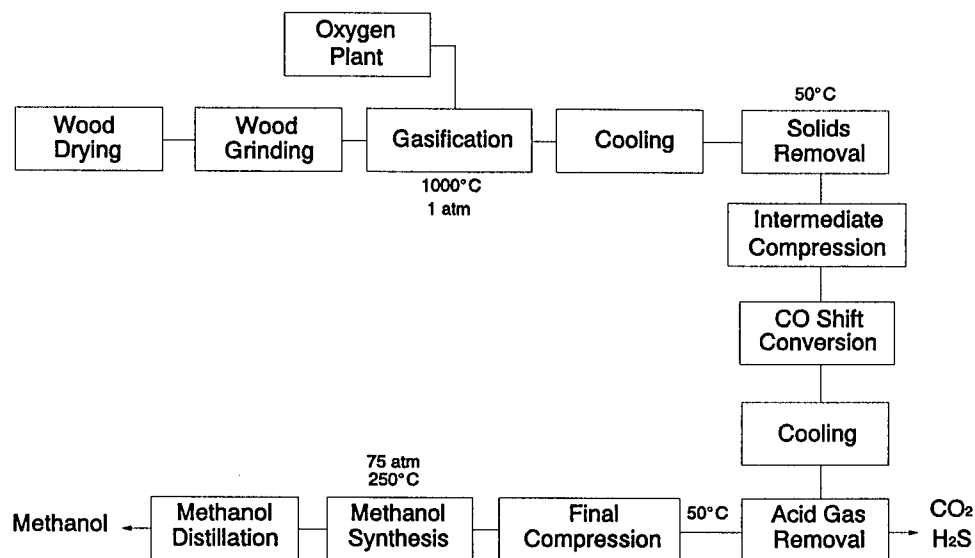
Figure 6.3   Koppers-Totzek gasification with low pressure methanol synthesis.

Each grinder train feeds a Koppers-Totzek gasifer. This gasifier, licensed by Krupp-Koppers of Germany as the GKT process, is an atmospheric, entrained bed reactor originally developed for use on coal (Figure 6.4). Because the gasification takes place at very high temperatures (1225 K) only very short residence times are required. Unfortunately, as mentioned above, in order to obtain complete reaction in the very short residence time, a very small particle size feed is required.

Table 6.2 shows the operating conditions, yield and product gas composition for the K-T gasifier as well as the IGT and BCL gasifiers which will be described in the following sections. Because the K-T gasifer has a very high operating temperature, it produces a gas with very little methane and virtually no higher hydrocarbons. Thus, there is no need for a reforming step to convert methane (an inert in the methanol synthesis process) into carbon monoxide and hydrogen. However, the H_2/CO ratio of the gas produced by the gasifer is low, and it is necessary to run the water-gas shift to produce additional hydrogen. When corrected to account for the potential value of the hydrocarbons, we see that the dry gas yield (a crude measure of the ability
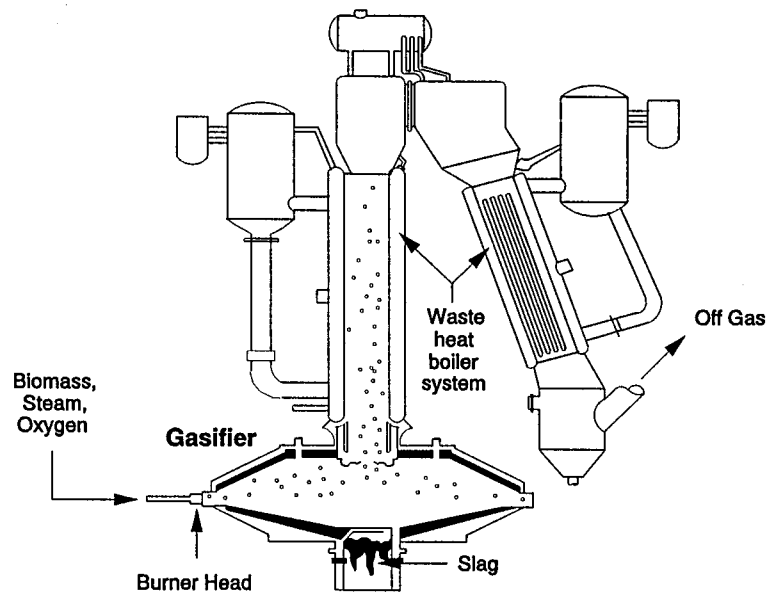
Figure 6.4 Koppers-Totzek gasifer schematic.

to produce methanol) is slightly lower than that for the other two gasifiers.

Oxygen is supplied to each gasifer by a separate cryogenic oxygen plant. Each oxygen plant is large (510 tonne oxygen/day), and therefore has a relatively low capital cost per unit of oxygen production.

After leaving the gasifier, the product gases at roughly 1,000°C are cooled to roughly ambient temperature in a heat exchanger/waste heat boiler so that conventional particulate removal technology can be employed and to minimize the work required in the compressors. The gases are then compressed and sent to the water gas shift reactor where CO is reacted with water to produce the hydrogen needed in the methanol synthesis process at 400°C.

The gas from the shift converter is again cooled to near room temperature and the acid gases (CO_2 and any H_2S) are removed by a Catacarb (Benefield) unit. This unit absorbs the acid gases in an aqueous stream of potassium carbonate.

The major processing equipment for methanol synthesis consists of a zinc oxide guard bed, syngas compressor, and methanol synthesis reactor, and the methanol recovery distillation columns. A typical Lurgi methanol synthesis process is shown in Figure 6.5. The synthesis gas is compressed and preheated and flows though a zinc oxide guard bed (not shown) which removes any final traces of H_2S which might poison the catalyst. The gases enter the synthesis reactor at 50 atmospheres pressure and 230°C. Because thermodynamic equilibrium is reached, only 50% of the synthesis gas is

Table 6.2   Operating characteristics of Koppers-Totzek, Institute of Gas Technology and Battelle Columbus gasifiers.

|	Koppers - Totzek[a]	IGT[b]	Battelle Columbus[c]
Gasification medium	steam, oxygen	steam, oxygen	steam
Gasifier heating mechanism	Oxygen blown	Oxygen blown	circulating heated sand
Temperature, K	1255	1255	1049
Pressure, MPa	0.1013	3.44	0.1013
Dry Gas Production Nm^3/metric ton	1347.5	1065.8	1027.2
Steam, kg/kg dry wood	0.3	0.3	0.61
Oxygen, kg/kg dry wood	0.56	0.3	0.0
Dry Gas Composition, Mol %			
H_2	36.2	30.9	30.6
CO	44.4	19.8	41.2
CO_2	19.1	36.2	10.9
CH_4	0.3	13.1	14.0
C_2	---	---	3.3
H_2/CO	0.82	1.56	0.74
Dry Gas (normalized for CH_4 + decomposition), Nm^3/metric ton	1360	1485	1510

[a] Chem Systems 1984
[b] Evans et al. 1988
[c] Feldmann et al. 1988

converted to methanol. Therefore, the product gases are cooled and the methanol separated out. A small amount of the gases are purged, and the methanol is purified by distillation. The unreacted gases are recycled and mixed with fresh feed.

The important operating parameters for the process are summarized in Table 6.3. The important feature is that compared to the commercial and pilot scale ethanol processes, the gasification-methanol synthesis process is quite efficient. This is because the thermochemical process makes use of the entire feedstock, not just the cellulosic fraction (which accounts for only about 42% of the energy content of the wood).
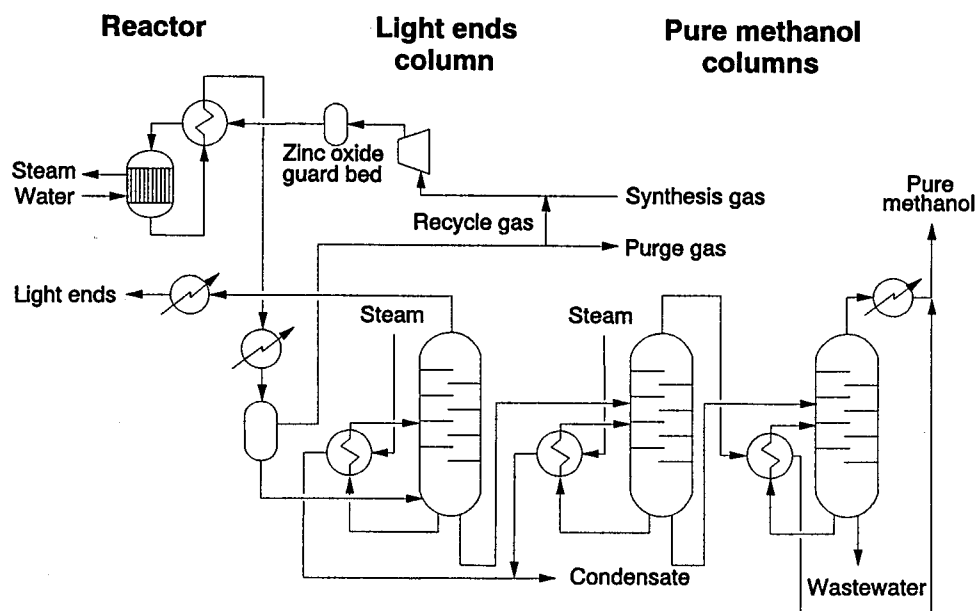
Figure 6.5 Processing schematic for the Lurgi low pressure methanol synthesis process.

Table 6.3 Yield and efficiency for the K-T - low pressure methanol synthesis process.

Products	
Methanol	329 E6 liter/year 87 E6 gallons/year
Overall Energy Efficiency	
Methanol	40.3%

6.3.2 Process Economics

Capital Investment. A breakdown of the capital investment by process area is shown in Table 6.4. As we saw above, the process is quite complicated, and therefore has an extremely high capital investment of $325 million. This is equivalent to $0.99/annual liter ($3.74/annual gallon) or $62.4/annual GJ. The largest single cost in the process is the gasifier. While this is not true for the more advanced cases, the Koppers-Totzek gasifer is an older design which has a relatively low productivity (m^3 gas produced/m^3 reactor volume-hr), and also has a more complex and costly design than the gasifiers used in the latter systems. The next largest contribution to the process cost (excluding the utilities section) is the oxygen plant. Because the K-T gasifier requires 0.56 tonne of oxygen per tonne of biomass, the oxygen plants are quite large and expensive. The feed preparation section is also relatively expensive because the K-T gasifer requires very small and very dry feedstock

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in order to complete the entrained bed gasification process in the allotted time. Because the K-T gasifier operates at high temperature, it produces little methane or tars, and the gas clean-up processes are inexpensive. However, because the entire product gas stream is cooled from 1000°C to room temperature, heated back to 400°C to run the water-gas shift reaction and cooled again to remove the acid gases, significant costs are incurred for heat exchange (the continual heating and cooling also reduces the process efficiency). Also, because the gasifier operates at atmospheric pressure, it is necessary to compress the entire product gas stream to roughly 50 atm. This creates both a capital and an operating cost. The actual cost of the methanol synthesis process is quite small.

Table 6.4 Capital investment for the Koppers-Totzek - low pressure methanol synthesis process.

Section	(million $)
Feedstock handling	38.3
Oxygen Plant	49.9
Gasification	97.5
Shift Conversion	0.8
Acid Gas Clean-up	11.1
Gas Compression	10.9
Methanol	21.4
Utilities, Offsite	57.4
Land, Owners costs, fees, profit, start-up costs	37.3
Total Cost	**324.6**
Capital Investment/ Unit of Annual Production	**$0.99/liter-yr $3.73/gallon-yr $62.4/GJ-yr**

Cost of Production. The cost of production estimate is shown in Table 6.5. By far the most important point is that charges related to the capital investment (return on investment and depreciation) account for two-thirds of the entire cost of production. Unlike the ethanol processes, the contribution of the feedstock cost to the cost of production is relatively small. This is because even though the efficiency of the individual thermochemical conversion processes are not as large as those of the biochemical processes, they operate on all of the feedstock, while the commercial- and pilot-scale ethanol processes convert only the cellulose (42% of the energy content of the feedstock) into ethanol.

In light of the dominant role of capital investment in the cost of production, the most important issue in improving biomass to methanol processes is to simplify the process (eliminate processing steps) in order to reduce the capital investment. Because the yield is already two thirds of that which is theoretically possible, yield improvements are somewhat less influential in reducing the cost of production. (In contrast, because of the low yields in the commercial and pilot scale ethanol processes, yield improvement was the most important issue for biochemical processes, while the reduction in capital investment was the secondary issue.)

Table 6.5   Cost of production summary for the Koppers-Totzek low-pressure methanol synthesis process.

|	¢/liter	$/gallon	$/GJ
Raw Materials			
Wood	9	32.18	5.72
Chemicals	0.16	0.60	0.10
Utilities			
Electricity	0.6	2.21	0.40
Cool Water	0.01	0.04	0.01
Feedwater	0.01	0.05	0.01
Labor	0.3	1.04	0.20
Maintenance	2.4	9.0	1.52
Overhead	2.3	7.0	1.50
Insurance, Property taxes	1.8	5.60	1.14
Total annual operating costs	**15.2**	**57.6**	**9.65**
Total capital charges (@30%)	**29.6**	**111.9**	**19.01**
Cost of Production	**44.8**	**169.6**	**28.50**

1 GJ = 0.948 MMBtu

6.4   Pilot Scale: Institute of Gas Technology (IGT)/Chem Systems Liquid Phase Methanol (LPMEOH) Synthesis

The process described in this section uses the IGT "Renugas" gasifier, coupled with the Chem Systems-Air Products liquid-phase methanol synthesis process. (The IGT gasifier is also quite similar to the high temperature Winkler (HTW) gasifier, which is run at the 24 dry tonne/hr at the Oulu ammonia plant in Finland.) Both the gasifier and the methanol synthesis processes have been demonstrated at the 10 ton/day scale or larger. This system incorporates several improvements over the previous process. The gasifier has a higher volumetric productivity and is less complex than the K-T gasifier, and therefore is less expensive. As a fluidized bed unit, considerably less drying and size reduction is needed. Because the gasifier operates at high pressure, the cost of compression is reduced. However, the unit produces a slightly higher concentration of methane and higher hydrocarbons. By converting these in a reformer to additional CO and H_2, the yields can be increased, however, these require an additional capital investment not found in the previous case. The liquid-phase methanol process provides better temperature control, and somewhat higher per pass

conversions than current processes. The analysis in this section is based on the same Chem Systems (1989) engineering study as the previous case.

6.4.1   Overall Process Design

The process flow schematic for the IGT Liquid-Phase Methanol Synthesis process is shown in Figure 6.6. In order to facilitate comparison of this process with the previous process, the operations used in this process are shown with solid lines in Figure 6.6, while the operations which have been eliminated are shown inside dashed boxes.
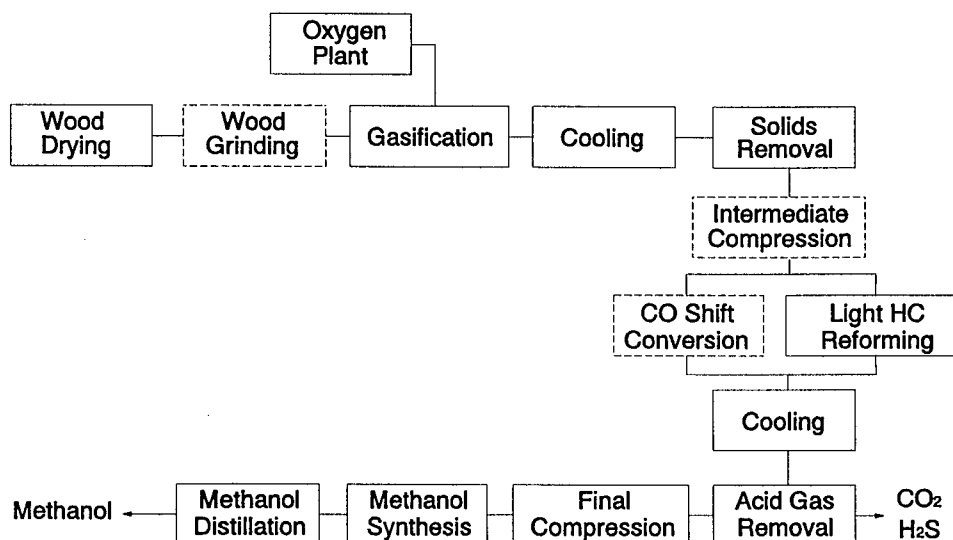
Figure 6.6   Schematic of the IGT liquid-phase methanol synthesis process.

In this process, whole green chips from the woodpile are dried to 15% moisture (which is much easier to achieve than 5% moisture), and fed directly (without grinding) to the gasifier through a pressurized lockhopper.

The IGT gasifier (Figure 6.7) has been developed specifically for biomass, and is a steam-oxygen blown fluidized bed gasifier. The gasifier has been operated at pressures of up to 24 atmospheres. The biomass is fluidized along with alumina spheres, which act as a heat reservoir and help to maintain even fluidization over a wide range of feed rates. As both the IGT and the K-T gasifiers are oxygen blown, they have similar gas outlet temperatures. However, because the IGT gasifier is operated at high pressure, the methane content of the outlet gases is considerably higher (Table 6.2 above), and a reforming unit is needed downstream of the gasifier to convert the methane into CO and H_2. While this slightly increases the yield, this step requires a large capital investment. The pressurized operation of the gasifier is an advantage because the energy required to introduce

incompressible solids into a pressurized gasifier through a lockhopper is much less than the energy needed to compress the large quantities of gases which are produced during the gasification process.
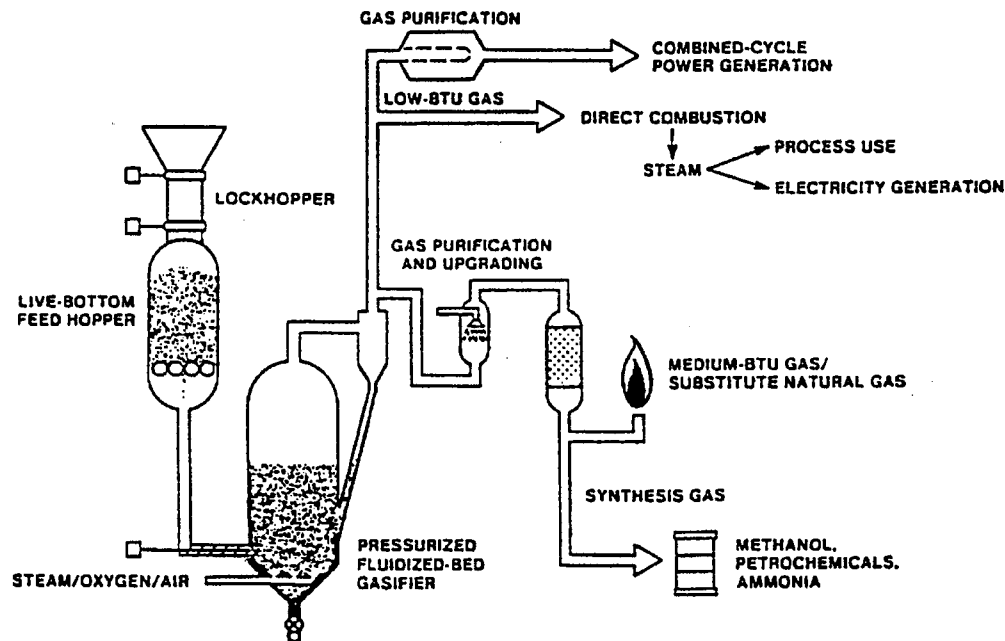

Figure 6.7   IGT gasification system.

After leaving the gasifier, the hot (1,000°C) gases are cooled to 50°C and any entrained solids are removed. Because the gasifier was operated at pressure, there is no needed for the intermediate compression step used in the previous process, and the gases are reheated and sent directly to the reformer. In the reformer, the methane is reformed with steam over a nickel catalyst to produce additional CO and H_2. After reforming, the gases are again cooled and the acid gases (CO_2 and any H_2S present) removed in the Catacarb unit.

The gases are further compressed from 25 to 100 atmospheres and sent to the methanol synthesis process. Water is removed by condensation, and the gases are passed though guard beds to remove any traces of sulfur or metal carbonyls which might be present in the gases. The fresh syngas is combined with the unreacted recycle gas, and enters a reactor which contains a slurry of catalyst particles entrained in an inert oil. The heat of reaction is absorbed by the slurry and released by exchange with boiler feed water through an internal tube bundle, producing intermediate pressure steam. This very efficient heat exchange process results in improved temperature control and therefore slightly increased yields (yields decrease with increasing temperature). The hot gases leaving the reactor interchange heat with the feed gas and the methanol is removed by condensation. The

condensed methanol is purified by distillation, and the unreacted gases are recycled back through the process.

The important operating parameters for the process are summarized in Table 6.6. The important feature is that the conversion efficiency of the process is increased by 15% (from 40% to 45.4%) compared with the commercial "K-T" case.

Table 6.6 Yield and efficiency of the IGT gasifier - liquid phase methanol synthesis. *feed rate = 1818 dry tonne/day*

Products	
Methanol	384 E6 liter/year 102 E6 gallons/year
Overall Energy Efficiency	
Methanol	45.4%

6.4.2   Process Economics

Capital Investment. The breakdown of the capital investment by process area is shown in Table 6.7. The capital investment is considerably lower than in the previous case ($240 million vs.$ 325 million), and the capital investment per unit of annual production is even lower ($39/annual GJ vs. $62/annual GJ) due to the increase in process efficiency and annual production. The cost of the wood receiving and preparation area is reduced by 50% because the drying requirements are not so severe, and because there is no longer a need to grind the feedstock to minus 30 mesh. The oxygen plant is slightly less expensive (but not greatly so) because the IGT gasifier uses 0.3 tonne oxygen/tonne biomass, compared with the 0.56 tonne/tonne used in the K-T gasifier. The gasification system is less expensive because the IGT gasifer has a better volumetric productivity and a simpler design. The cost of upgrading the raw synthesis gas is significantly larger in the case of the IGT gasifer, which makes a considerable amount of methane. The reformer operates at 800°C, using tubes built from very expensive high alloy steels, and uses a very large amount of nickel catalyst. While the added cost is more than offset by the added methanol production, the reformer accounts for more than 10% of the total plant investment. The acid gas removal system is identical to that in the previous system. Because the IGT gasifier is coupled with a Liquid Phase Methanol Synthesis unit which operates at a higher pressure than the standard system used in the previous case, the compression costs are the same as in the previous case, even though the gasifer is operated at elevated pressure. The methanol synthesis, utilities, and miscellaneous owners costs are similar for the two systems.

Table 6.7   Capital investment for the IGT liquid phase methanol synthesis process.

Section	million $
Feedstock Handling	17.1
Oxygen Plant	43.3
Gasification	29.4
Solids Removal	0.8
Reformer	31.9
Acid Gas Removal	11.8
Gas Cooling	2.0
Gas Compression	8.2
Methanol Synthesis	24.2
Utilities, Offsite	42.2
Land, Owners costs, fees, profit, start-up costs	29.7
Total Cost	**240.6**
Cost/Unit of annual production	**$0.62 $/liter-yr** **$2.34/gallon-yr** **$39.1/GJ-yr**

Cost of Production. The cost of production estimate is shown in Table 6.8. The methanol cost is significantly reduced, primarily because the reduced capital investment, and secondarily because of the increased process efficiency. In spite of these advancements, there remains considerable room for improvement.   In particular, the oxygen plant still requires a large investment, the gasifier is still expensive, and the raw gases from the gasifer are still heated and cooled several times, increasing cost and reducing efficiency.

6.5   Battelle-Columbus Gasifier with Low Pressure Methanol Synthesis

The base case and conceptual process described in this section both make use of the Battelle-Columbus (BCL) indirectly fired gasifier, which allows elimination of the oxygen plant. These processes also make use of hot gas clean-up technology developed for coal gasifiers to eliminate the penalties resulting from the need to repeatedly heat and cool the syngas.   BCL gasifiers (15 and 25 cm diameter) have been operated with feed rates of 20 tonne/day. As with the K-T system, this process design is based on the use of standard low pressure methanol synthesis technology. The analyses of the BCL based system are based on an analysis carried out by Bain in 1991 at the United States National Renewable Energy Laboratory (NREL) (Wyman, Bain et al 1993).

Table 6.8 Cost of production summary for the IGT liquid-phase methanol synthesis process.

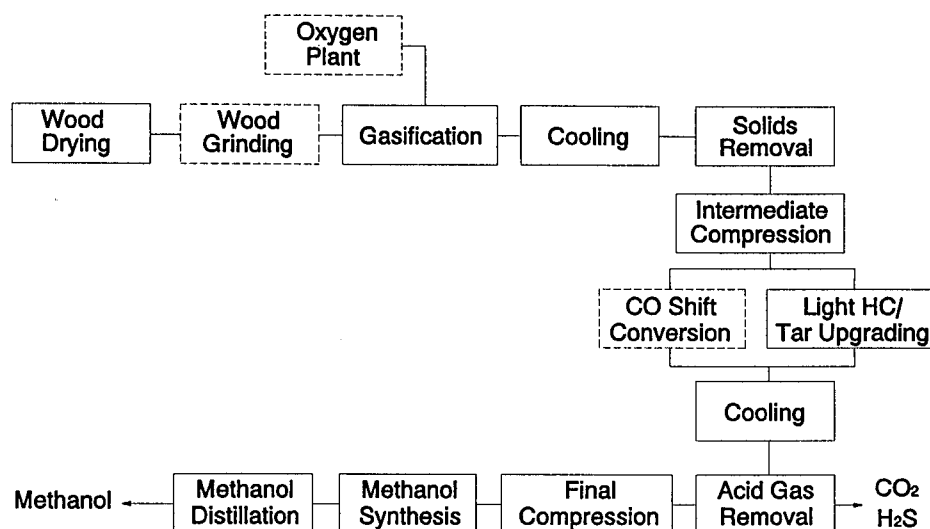|	¢/liter	¢/gallon	$/GJ
Raw Materials			
Wood	7.3	27.6	5.03
Chemicals	0.45	1.70	0.28
Utilities			
Electricity	0.6	2.2	0.40
Steam, 1MPa	1.3	4.8	0.83
Steam, 5MPa	-1.6	-6.1	-1.02
Cool Water	0.04	0.14	0.03
Feedwater	0.07	0.26	0.04
Fuel	0.3	1.04	0.20
Labor	0.23	0.9	0.15
Maintenance	1.5	5.7	1.05
Overhead	1.3	4.7	0.82
Insurance, Property taxes	0.9	3.7	0.60
Total annual operating costs	**12.3**	**46.4**	**8.01**
Total capital charges (@30%)	**19**	**71.1**	**12.10**
Cost of Production	**31.1**	**117.6**	**20.10**

1 GJ = 0.948 MMBtu

6.5.1 Process Design

The process design for the BCL/low-pressure methanol synthesis system is shown in Figure 6.8. (Again, unit operations which have been eliminated are shown in dashed boxes to facilitate comparison between the different processes.) The feedstock is dried to 15% moisture and fed directly (without grinding) to the atmospheric pressure, fluidized bed gasifer.

The BCL gasifier is a low-pressure indirectly heated design in which the char produced by the steam pyrolysis of the biomass is removed from the gasifier, and burned in a separate fluidized bed combustor to provide the heat necessary to run the pyrolysis reactions (Figure 6.9). The heat is transferred from the combustor to the gasifier by a circulating bed of sand. The sand is heated directly in the fluidized bed combustor, carried out at the top of the combustor, and separated from the hot gases with a cyclone. The hot sand is fed by gravity into the bottom of the gasifer, where it transfers its heat to the pyrolyzing biomass. After giving up its heat, the sand is swept from the

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Oxygen Plant

Wood Drying — Wood Grinding — Gasification — Cooling — Solids Removal

Intermediate Compression

CO Shift Conversion | Light HC/ Tar Upgrading

Cooling

Methanol ◄— Methanol Distillation — Methanol Synthesis — Final Compression — Acid Gas Removal — CO_2 H_2S

Figure 6.8 Battelle-Columbus low-pressure methanol synthesis process schematic.

top of the gasifer, separated from the raw syngas in a cyclone, and returned to the combustor to repeat the cycle. Because the sand carries the heat from the combustor to the gasifer, and the combustion gases from combustor do not enter the gasifier, it is possible to carry out the combustion process with air instead of oxygen. Thus, the capital and operating costs of the oxygen plant required in the other systems are eliminated.

Because the temperature in the BCL gasifier is lower than that in the previous gasifiers, the system produces large amounts of methane and higher hydrocarbons. Although these must be reformed to produce CO and H_2, the methanol yield after reforming is higher than that of the previous systems.

The raw syngas from the gasifier is quenched, and the tars and solids are separated. It is assumed that the tars are recycled to the gasifer and converted to syngas (although this has yet to be shown demonstrated in practice). The gases are then compressed and reheated, and sent to the reformer/shift reactor, where the reforming of the methane and higher hydrocarbons and the water gas shift reaction are carried out simultaneously. The remainder of the process is identical to that described in the previous section, and consists of a cooling section, acid gas removal, final compression, and methanol synthesis and distillation. The annual production and efficiency of the process are shown in Table 6.9. The most important point is that the efficiency of the process is increased by 18% (from 45% to 53%).

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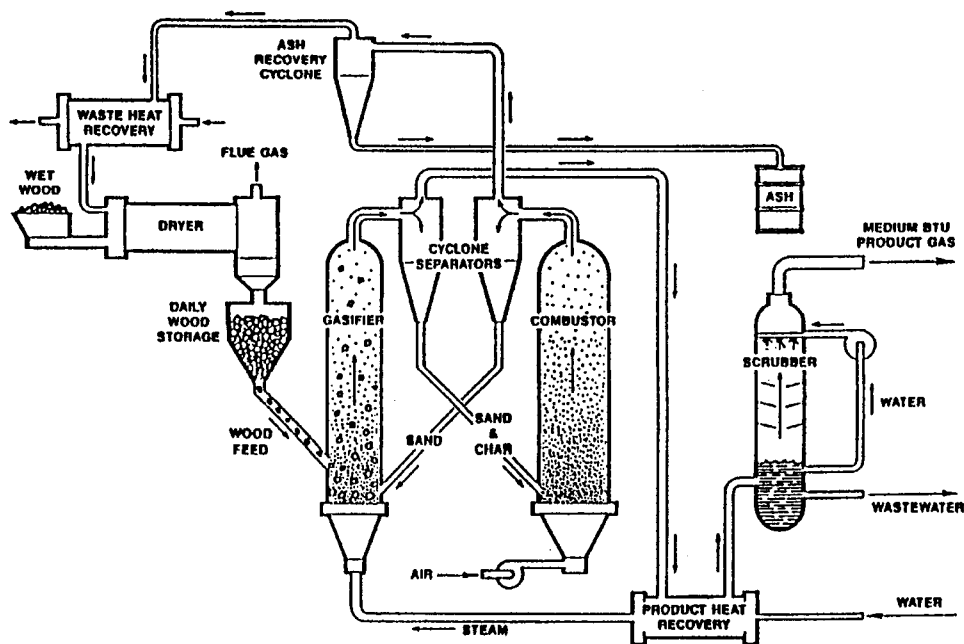
Figure 6.9   Battelle-Columbus gasification system.

Table 6.9   Yield and efficiency for the Battelle-Columbus gasifier - low pressure methanol synthesis process.

Products	
Methanol	469 E6 liter/year 124 E6 gallons/year
Overall Energy Efficiency	
Methanol	53.5%

6.5.2   Process Economics

Capital Investment. The capital investment is 17% lower than in the previous case, and the investment per annual liter production is reduced by 32% (Table 6.10). The major change is the elimination of the cryogenic oxygen plant, which contributed $43 million to the cost of the previous system. Also, the cost of the gasification system is somewhat reduced.

Cost of Production. The cost of production ($0.23/liter or $0.88/gallon) is still dominated by the capital investment, which accounts for 55% of the total

production cost. The second most important cost component is the cost of the wood feedstock, which contributes 25% of the total costs (Table 6.10).

In light of the importance of the capital investment, the final case described below incorporates a variety of process improvements adapted from coal gasification technology to reduce the capital investment.

6.6 Advanced System: Battelle-Columbus Gasifier with Low Pressure Methanol Synthesis (Advanced Case)

This advanced case of the BCL-low pressure methanol synthesis process incorporates hot-gas clean-up technology developed for coal gasification systems to prevent the cost and efficiency loss involved in repeatedly heating and cooling the syngas. The data for this section are taken from the analysis of Bain which also formed the basis of the previous section (Wyman, Bain et al 1993).

6.6.1 Process Design

The only major change in the design of the advanced case is the use of hot gas clean-up technology (Figure 6.10). In this system, the raw syngas from
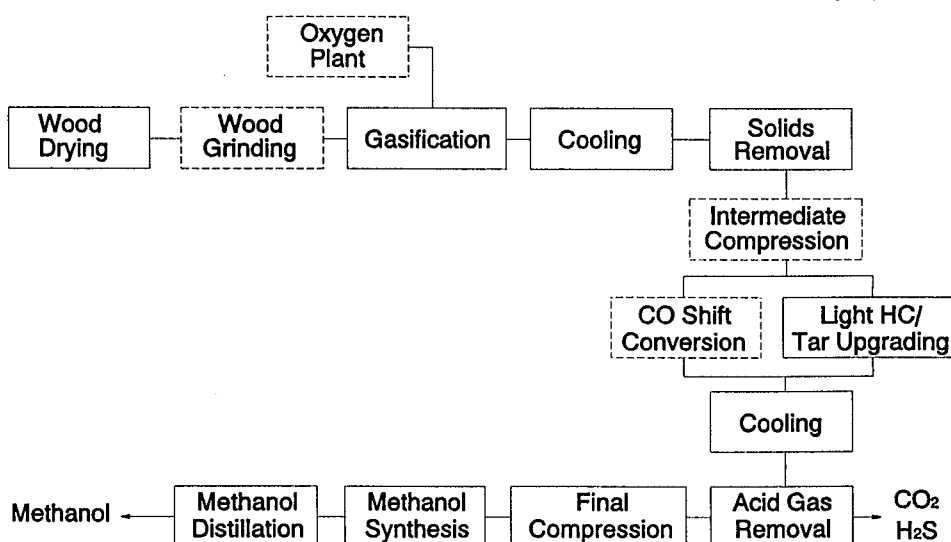
Figure 6.10 BCL low-pressure methanol synthesis with hot gas clean-up (advanced case).

the gasifier is taken directly to a catalytic reactor, where the tars, methane, and higher hydrocarbons are catalytically reacted to form additional CO and H_2. The capital cost savings come from the elimination of large heat exchangers. Also, in the previous designs the raw syngas was cooled and compressed, then reheated before entering the reformer. The cooling and compression resulted in much of the water being condensed out of the

Table 6.10 Capital investment for the Battelle-Columbus gasifier low-pressure methanol synthesis system.

Section	Million $
Feed	20.3
Oxygen Plant	0.0
Gasification	7.9
Gas conditioning	1.7
Reformer	41.3
Acid Gas Removal	11.6
Gas Cooling	0.0
Gas Compression	25.7
Methanol Synthesis	32.2
Utilities	35.2
Land, Owners, costs, fees, profit, start-up costs	23.2
Total Capital Investment	199.2
Cost/Unit of annual production	$0.42/liter-yr $1.59/gallon-yr $26.5/GJ-yr

syngas. As this water contains phenolics and other organics, it presents a major pollution problem. Also, because the reforming is carried out in the presence of a large excess of water, water was added back in the form of steam as the gases entered the reformer. By eliminating the cooling and compression steps, the steam from the gasifier does not condense out, eliminating the need to clean-up a water stream and reducing the utilities costs. The efficiency and annual production figures of this case are identical to the previous case (which were given in Table 6.9).

6.6.2   Process Economics

Capital Investment.The capital investment for the advanced (hot gas clean-up) version of the BCL low-pressure methanol synthesis process is reduced 20% by the elimination of heat exchangers, a simplification of the tar destruction/reforming/water gas shift reactors and the elimination of the need to condense water out of the raw syngas, clean up the heavily organic laden water, and then added the water back in the form of steam before the reformer.

Cost of Production. The reduction in the cost of production from $0.23/liter to $0.20/liter ($14.5 to $12.6/GJ) is due entirely to the reduction in the capital investment. It is interesting to note that the in spite of the reduction in capital

Table 6.11 Cost of production for the BCL gasifier low-pressure methanol synthesis process (base case).

	¢/liter	¢/gallon	$/GJ
Raw Materials			
Wood	6.0	22.62	4.01
Chemicals	0.0	0.0	0.0
Utilities			
Electricity	1.2	4.10	1.50
Steam 150 psig	0.0	0.0	0.0
Steam 40 psig	0.0	0.0	0.0
Cool Water	0.0	0.0	0.0
Feedwater	0.0	0.0	0.0
Other variable costs	0.7	2.60	0.44
Labor	0.2	0.73	0.12
Maintenance	0.9	3.64	0.60
Overhead	0.8	3.17	0.50
Insurance, Property taxes	0.6	2.41	0.40
Total annual operating costs	**10.3**	**39.28**	**6.54**
Total capital charges (@30%)	**13.0**	**48.28**	**8.30**
Cost of Production	**23.1**	**87.55**	**14.70**

1 GJ = 0.948 MMBtu

investment from the commercial K-T case to the advanced BCL case, the recovery and return of the capital investment is still the major contributor to the cost of production.

6.7 Additional Potential Improvements in the Production of Methanol from Biomass

There are several potential improvements in the production of methanol from biomass which have not been analyzed in the preceding sections. A few of the potential improvements are described below. An improvement particular to biomass-based processes is the development of a pressurized, indirectly heated gasifier (for example, a high-pressure version of the BCL gasifier). Such a system would require the use of lockhoppers between the gasifer and the fluidized bed combustor which would allow the sand to pass from an atmospheric pressure combustor to a high-pressure gasifer. This would reduce the cost of compression (as the introduction of solids biomass into a gasifier requires much less energy than compressing the many moles of gas which are produced during the gasification of the biomass).

Table 6.12   Capital investment for BCL gasification with low pressure methanol synthesis and hot gas clean-up.

Section	Million $
Feed	20.3
Oxygen Plant	0.0
Gasification	7.9
Gas conditioning	12.8
Reformer	0.03
Acid Gas Removal	11.6
Gas Cooling	0.0
Gas Compression	25.6
Methanol Synthesis	32.2
Utilities	27.6
Land, Owners, costs, fees, profit, start-up costs	20.0
Total Capital Investment	**158.2**
Cost/Unit of annual capacity	**$0.33/liter-yr $1.10/gallon-yr $20.8/GJ-yr**

Improvements to the methanol synthesis process would help not only biomass to methanol processes, but the existing major industry which converts natural gas and heavy hydrocarbons to methanol. Because the methanol industry is quite large, such research is ongoing worldwide.

An example of improved technology would be the development of methanol synthesis catalysts which are active at lower temperatures. Because the conversion of syngas to methanol is exothermic, the potential conversion increases rapidly as the conversion temperature is reduced. For example, a recently announced process under development at Brookhaven National Laboratory in the United States uses a liquid-phase catalyst to carry out the methanol synthesis at 100°C instead of the current 260°C. This would allow virtually complete conversion in a single pass, allow the use of air instead of oxygen in the gasification system, and eliminate the capital expenses and operating inefficiencies which come from the large recycle streams used in conventional processes (Stone and Webster 1990).

Another improvement to the methanol synthesis process itself would be the development of catalysts which are capable of carrying out methanol synthesis in the presence of large quantities of CO_2. Such a catalyst would eliminate the need for the acid gas removal system, and eliminate an entire process step.

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Table 6.13 Cost of production for the BCL gasifier low-pressure methanol synthesis process with hot gas clean-up.

|	¢/liter	¢/gallon	$/GJ
Raw Materials			
Wood	6.0	22.62	4.01
Chemicals	0.0	0.0	0.0
Utilities			
Electricity	1.2	4.10	1.10
Cool Water	0.0	0.0	0.0
Feedwater	0.0	0.0	0.0
Other variable costs	0.7	2.60	0.44
Labor	0.2	0.73	0.12
Maintenance	1.0	3.64	1.03
Overhead	0.9	3.17	0.60
Insurance, Property taxes	0.5	1.92	0.31
Total annual operating costs	**10.2**	**38.78**	**6.50**
Total capital charges (@30%)	**10.1**	**38.33**	**6.42**
Cost of Production	**20.4**	**77.11**	**13.10**

1 GJ = 0.948 MMBtu

6.8   Sensitivity Analysis

As the economics of both the biochemical ethanol production processes and the thermochemical methanol production processes are both dominated by the charges related to the capital investment, it is not surprising that the sensitivity analyses are quite similar (Figure 6.11). For methanol production, the effect of a ±33% change in the capital recovery factor changes the cost of production by 28% (as would a 33% change in the capital investment). On the other hand, a 20% reduction in feedstock cost would reduce the cost of production by only 4%.

The effect of the conversion facility size on the cost of production is shown in Figure 6.12. Because return on the capital investment is the dominant cost in the thermochemical processes, the methanol biomass to methanol process is relatively sensitive to plant size. A factor of 2.5 increase in scale reduces production costs by 15%, while a factor of 2.5 reduction in size increases the cost of production by 20%.
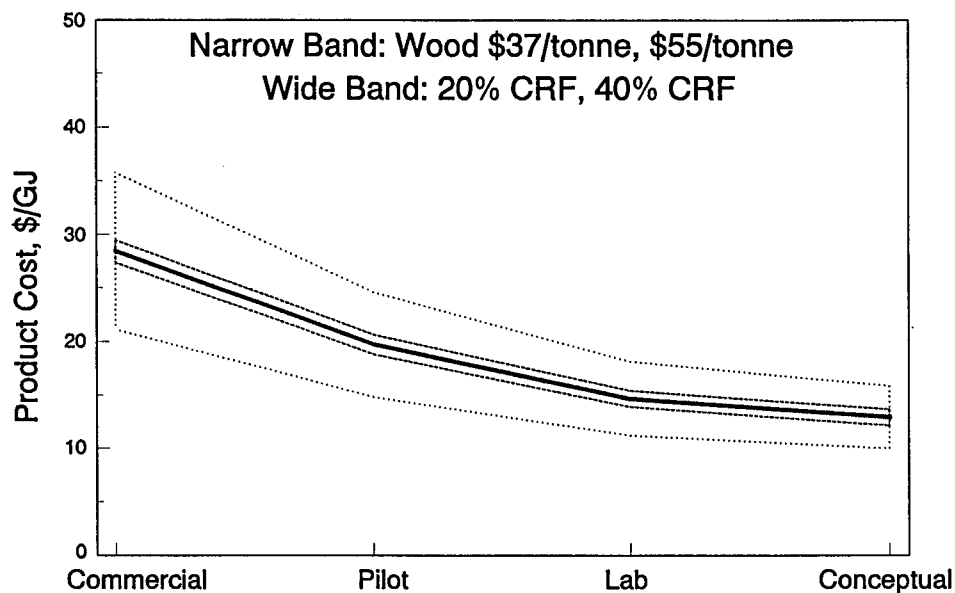
Figure 6.11   Sensitivity of the cost of methanol production to changes in the capital recovery factor and feedstock cost.
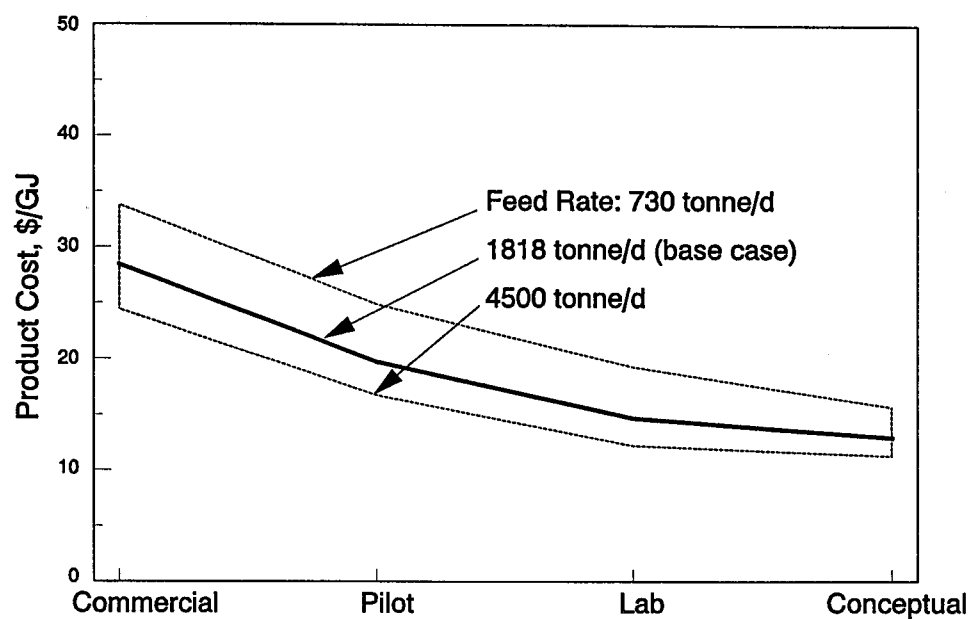
Figure 6.12 Effect of scale on the cost of thermochemical production of methanol from biomass.

6.9 Summary of the Thermochemical Conversion of Biomass to Methanol

The economics of the four different biomass to methanol cases are summarized in Figure 6.13. The cost of production ranges from $0.45/liter or $1.70/gallon ($28.5/GJ) in the commercially demonstrated case to a low of $0.20 liter or $0.77/gallon ($13.1/GJ) for the conceptual case. In all cases, the economics are dominated by the capital investment, which accounts for roughly 66% of the costs in the current case and 50% of the costs in the conceptual case.

The efficiency of the processes is near that theoretically possible. The processes based on partial oxidation gasification systems (K-T and IGT) have efficiencies of 40% and 45%, compared with a thermodynamic limit of roughly 52%. The indirect-fired steam gasification systems have an efficiency of 53%, compared with a theoretical limit of 58%. Thus, it is unlikely that gasification-based processes can have significantly higher yields than those shown in this report.
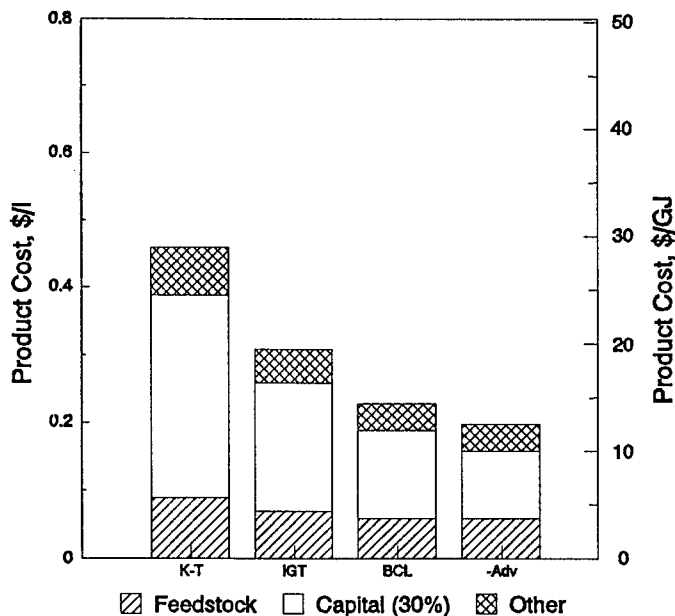
Figure 6.13 Economic summary of biomass to methanol processes.

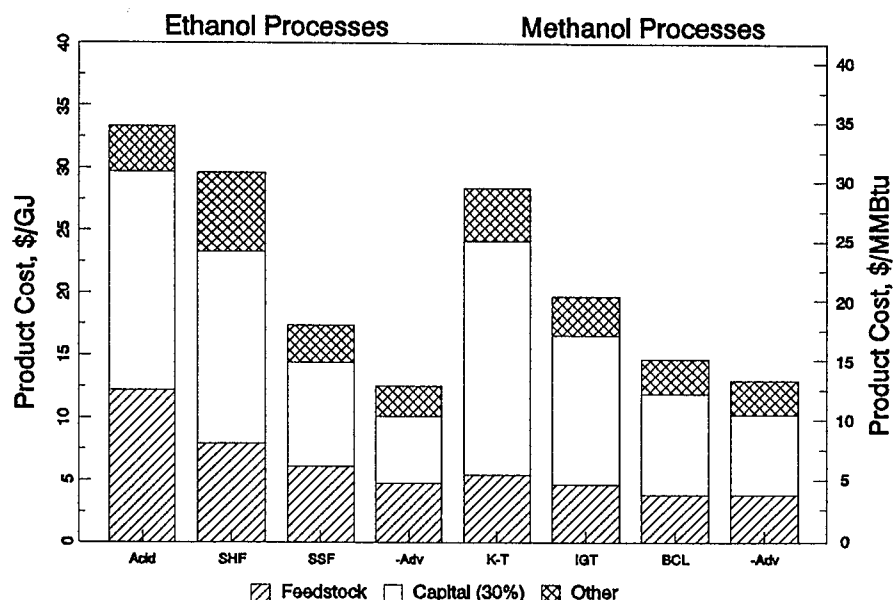# 7 Comparison of Methanol and Ethanol Production Processes

The cost of production of methanol and ethanol from biomass are shown on a volumetric basis in Figure 7.1, and on an energy basis in Figure 7.2. While comparisons between different ethanol processes or different methanol processes are customarily made on a volumetric basis, such a comparison is misleading when processes for producing the different fuels must be compared, as the fuels have different volumetric energy densities. Therefore, all comparisons in this section will be made on an energy basis.
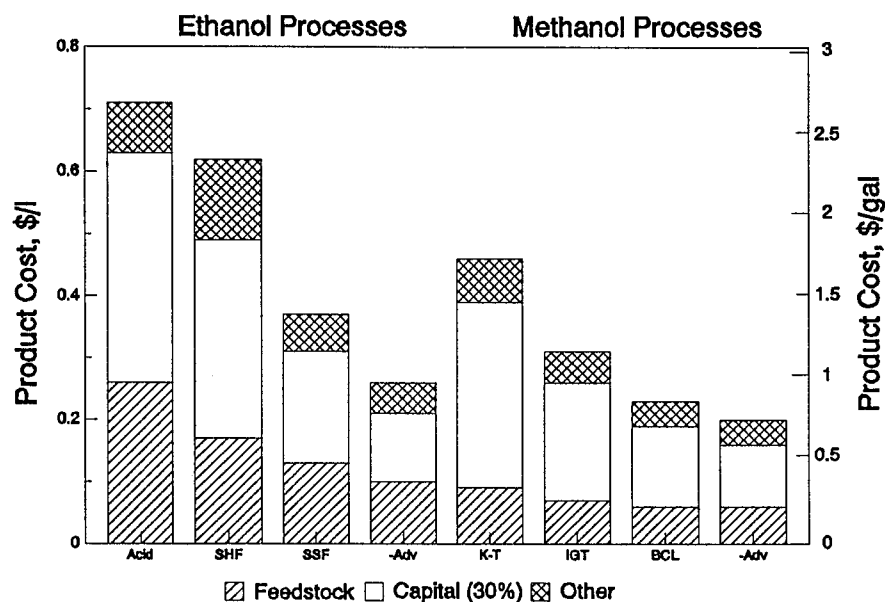
Figure 7.1 Comparison of the cost of production of methanol and ethanol on a volumetric basis.

The important conclusion of the analysis is for processes that have been demonstrated at the commercial and pilot scales, methanol production is considerably less expensive than ethanol production. However, for the laboratory-scale processes there is little difference, and for the "conceptual" processes which attempt to estimate the limits of process improvement, the economics of the methanol and ethanol production are virtually identical.

This result is a direct outgrowth of the basic nature of the biomass feedstock, and the fundamental characteristics of the two types of processing. The ethanol processes convert the carbohydrate fraction of the biomass (which accounts for roughly 60% of the energy content of the feedstock) to ethanol with an extremely high efficiency (roughly 85%, compared with a theoretical limit of 95%). Thus, the overall efficiency of converting biomass to ethanol is approximately 50%. In contrast, because of the temperature mismatch between the endothermic gasification process (which requires heat at

Figure 7.2 Comparison of the cost of production of methanol and ethanol on an energy basis.

1000°C) and the exothermic methanol synthesis process (which produces heat at only 230-300°C), the maximum efficiency of the thermochemical conversion process is only 52-58%. However, because the gasification process operates at high temperatures and converts all fractions of the biomass to simple molecules, such as CO, CO_2, H_2 and H_2O, from which the methanol is synthesized, the methanol synthesis processes can use all fractions of the feedstock, not just the carbohydrate fraction. A thermochemical process which achieves 90% of the theoretically possible 58% efficiency has a overall process efficiency of a little better than 50%. Thus, the ultimate efficiencies of the processes which produce methanol and ethanol from biomass are essentially identical.

The most important parameter in determining the cost of production is the efficiency with which the process converts the biomass into alcohol (Figure 7.3). We see that the efficiency of ethanol production rises from 20% for the percolation acid hydrolysis - glucose fermentation case, to 30% for the logen enzymatic hydrolysis - glucose fermentation process (because of the higher hydrolysis yield and the improvement in fermentation efficiency brought about by the reduction in toxic hydrolysis byproducts. The process efficiency increases to 39% when xylose fermentation is added, and to 50% as the process nears the theoretical limits. In contrast, the conversion efficiency of the Koppers-Totzek gasification - low pressure methanol synthesis process is a respectable 40%. Improvements in yield in the Institute of Gas Technology and Battelle-Columbus gasification processes bring this to 45% and 53%, again close to the theoretical limits. While yield is the most important parameter in both ethanol and methanol processes, it

plays less of a role in the discussion of methanol economics, simply because it starts from a higher base. The major reason that the commercial- and pilot-scale methanol technology has better economics than the ethanol technology is that the early ethanol technology makes use only of the cellulose fraction of the feedstock, and therefore has low conversion efficiencies. Ultimately, as discussed above, the methanol and ethanol economics are similar because the limiting conversion efficiencies are similar.
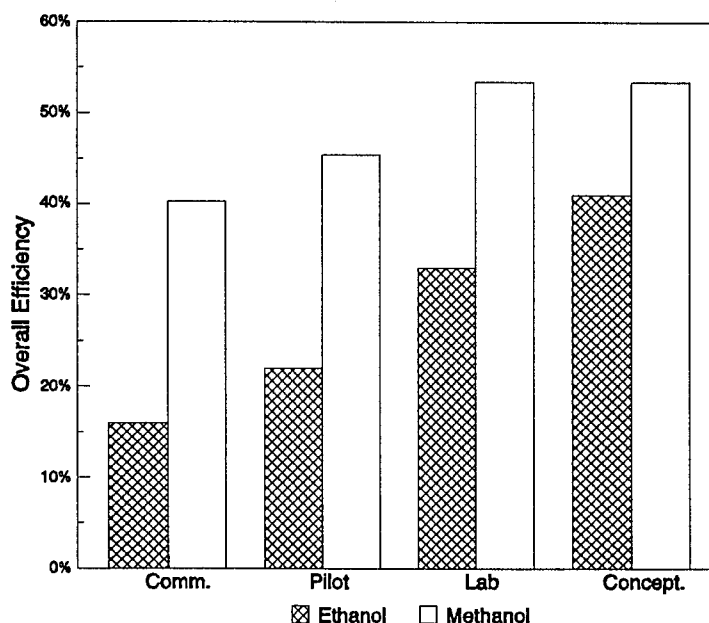
Figure 7.3 Efficiency (energy content of the fuel/energy content of the feedstock) for methanol and ethanol production processes.

Capital investment per unit of production is similar for the two processes (Figure 7.4). We see that the investment per unit of annual capacity is similar at all stages of development. There is no fundamental reason for this, it merely suggests that equivalent results can be achieved with slow processes which operate in large vessels at low temperatures and pressures and rapid processes which require only small vessels but operate at high temperatures and pressures. In the case of ethanol production, the reduction in capital cost/unit of annual production is caused primarily by increases in the process efficiency (which spreads a relatively constant investment over a larger production capacity). In contrast, the reduction in capital costs/unit of production for methanol is due to a reduction in the investment, and only secondarily to an increase in yield.

Several parameters, notably the size of the facility, the cost of the feedstock, and the capital recovery factor can have a marked effect on the economics of producing alcohol from biomass. Therefore, we carried used the data developed in the sensitivity analyses to determine whether changes in any of

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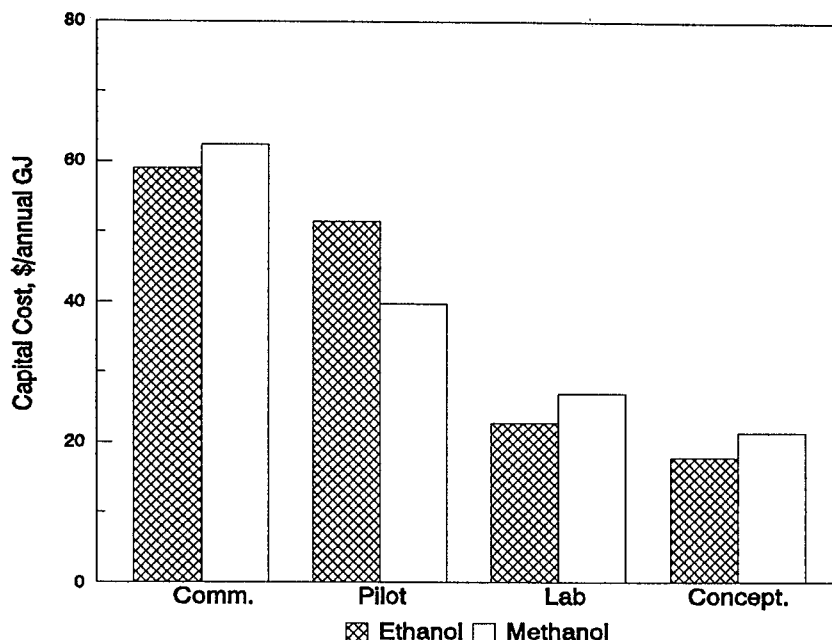
Figure 7.4 Capital investment per unit of annual production for methanol and ethanol conversion processes.

these parameters would alter any of the conclusions of the study. Figure 7.5 shows that the more capital intensive methanol production processes are more sensitive to plant size than the methanol processes (which improves the relative economics of methanol at large sizes and improves the relative economics of ethanol at small sizes). However, even when size of the plant is cut by a factor of 2.5 from 1818 tonne/day to 730 tonne/day, there is only a small (13%) difference between the production costs of the two types of process. Given the uncertainties of the cost of production estimates, this is not a significant difference.
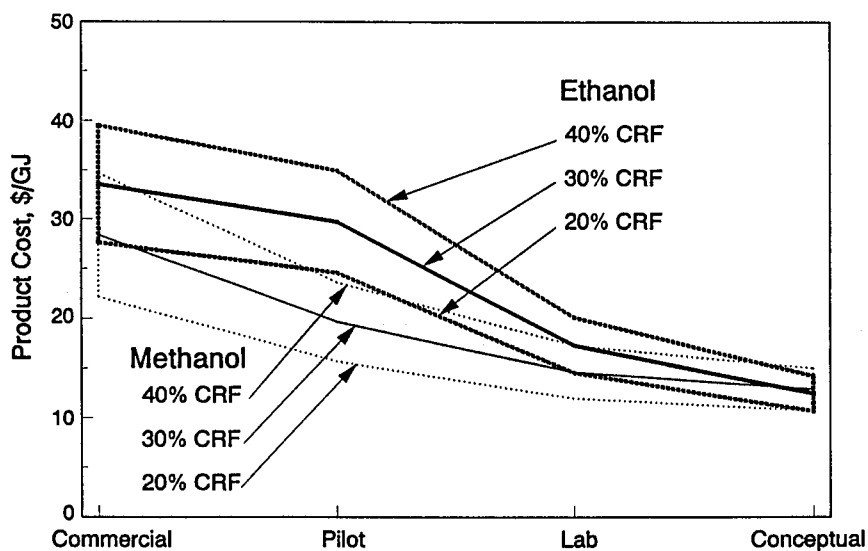
The effect of the capital recovery factor is shown in Figure 7.6. While the CRF has a greater effect on the methanol process than the ethanol process, there is no significant effect of CRF on the relative economics of the two processes.

The effect of feedstock cost is shown in Figure 7.7. Because the feedstock accounts for only 30% to 35% of the total cost of production, a 22% change in feedstock cost results in only a 7% change in the total cost of production. As the advanced methanol and ethanol processes have similar efficiencies, a change in feedstock cost affects both equally, and has no effect on the relative economics.

In conclusion, the near-term methanol production processes have superior economics, due primarily to their high conversion efficiencies. However, in the longer term, the production costs for methanol and ethanol should be
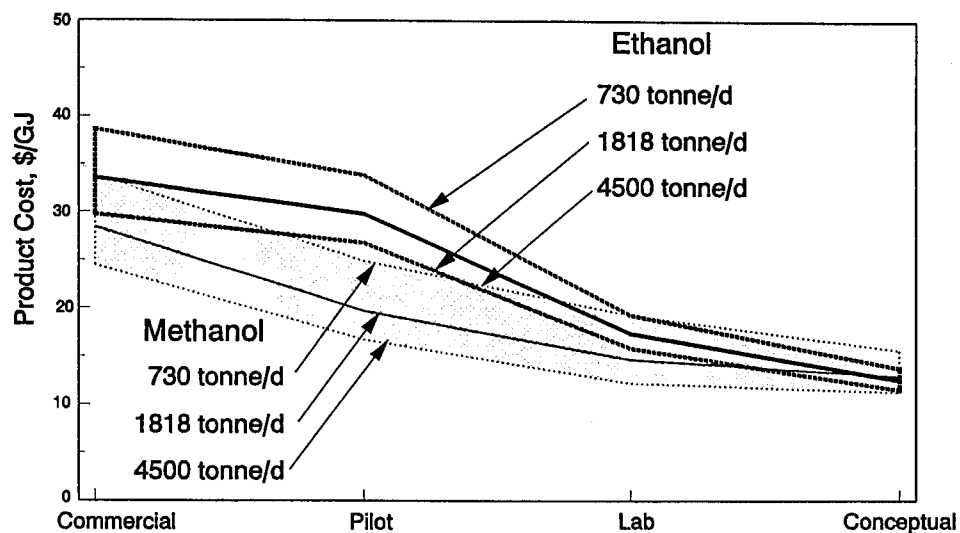
Figure 7.5   Sensitivity of methanol and ethanol production costs to size of the process plant (measured in dry tonne feedstock processed/day).

Figure 7.6   Sensitivity of methanol and ethanol production costs to the capital recovery factor (CRF).

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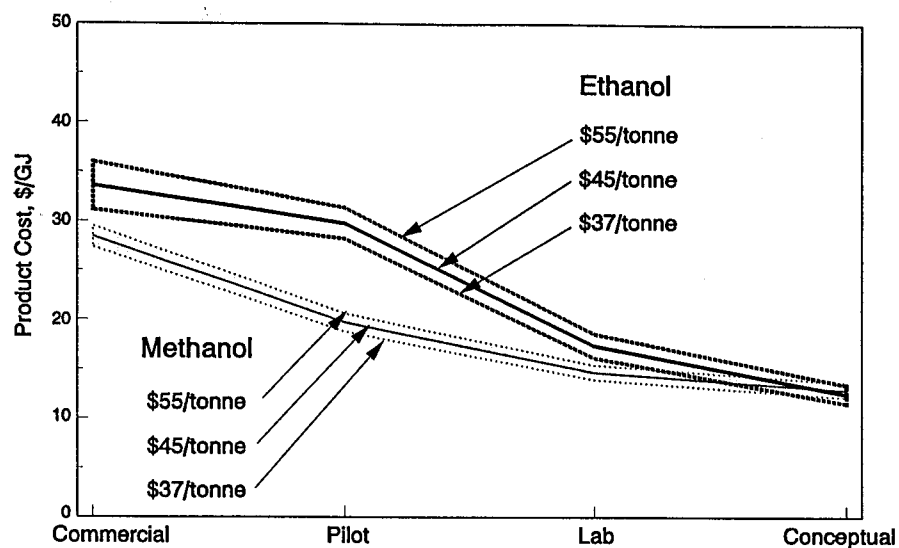
Figure 7.7 Sensitivity of methanol and ethanol production costs to the feedstock cost ($/dry tonne).

similar, as the limiting yields of the two types of processes are essentially identical.

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